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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
by STEPHEN LAWROSKI and ASSOCIATES,
ARGONNE NATIONAL LABORATORY

● JAN. 1962
● VOLUME 5
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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., I. G. Dillon, P. Fineman, J. Fischer, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, W. B. Seefeldt, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Transporting Irradiated Fuel Elements

Since the construction of both foreign and domestic nuclear reactors is steadily increasing, and a number of reactors soon will be ready for refueling, the overseas and overland transportation of irradiated fuel elements from reactor sites to fuel-processing plants will be necessary on an increasing scale. Under the "Atoms for Peace" program, the U. S. Government will be providing fuel for some 68 reactors and critical assemblies in 24 countries. By August 1961 special nuclear material had been supplied and shipped to some 57 foreign reactors. The total enriched uranium transferred overseas for research and reactor programs has been some 1700 lb, which is only part of the 100,000 lb allocated. This quantity will be increased considerably after the completion of several nuclear power reactors in Italy, Germany, and Japan, with fuel loadings of approximately 1000 to 2000 lb of contained U^{235} in low-enrichment uranium every two years. The majority of the foreign reactor operators who have leased or purchased fuel from the United States will be returning irradiated elements for processing at AEC facilities at Savannah River or at Idaho Falls. Shipments of irradiated fuels will commence around the first part of 1962 and will come from France, Germany, Sweden, and Denmark at the rate of some 600 lb of U^{235} per year, involving on the average about one shipment per month. With the advent of the foreign power programs in 1964 and with the lack of overseas processing facilities, the shipments are expected to increase to a rate of four per month involving some 3000 lb of U^{235} per year.[1]

In general, the overseas transportation of special nuclear materials in the past has been without incident, but there has been an increasing trend toward reluctance on the part of shippers to accept materials for overseas shipments. No doubt this has been the result of publicity on indemnity and the introduction in early 1960 of an exclusion clause by London Underwriters, one of the major insurance companies for ocean shipping lines. Under this exclusion clause the shipper would be required to take out additional insurance, amounting in most cases to approximately $5000 to $10,000 on each shipment of fissionable materials regardless of the quantity. This would result in very high cost for ocean transport.[1]

Since the airlines do not have exclusion clauses in their insurance policies, most airlines have been willing to handle special nuclear material, provided that the material being shipped is packaged safely and is accompanied by a certificate of air worthiness. In late 1960, however, the Sabena and KLM airlines placed an embargo on shipping special nuclear material, and all fuel materials being shipped to Belgium and the Netherlands by way of these two airlines have been refused. Shipments have been made, however, by means of airlines that do not have this embargo.[1]

The overland transportation of nuclear materials has also encountered some difficulties. The absence of suitable insurance has caused a number of bridge, tunnel, and toll highway authorities to restrict or prohibit the movement of nuclear or radioactive materials over their facilities. Since toll routes tend to skirt areas of high population and traffic density, these routes are often preferred for carrying nuclear materials.[2]

In addition to the insurance problem, the AEC sees several specific needs that must be provided before transportation problems can be solved. These are education of the transporta-

tion industry in handling and charging for nuclear shipments; standardization of shipping containers for high-level radioactive materials; and updating of pertinent regulations. To define and help resolve these problems, the AEC is conducting a series of conferences with transportation authorities, shippers, and the insurance industry.

The International Atomic Energy Agency (IAEA) has recently adopted comprehensive regulations for transport of radioactive and fissionable material, designed both for IAEA operations and as a model for national and international rules.[3] The IAEA rules may have an important influence on the future course of U. S. nuclear transport regulations.

The AEC has had under consideration since March 1960 a proposed regulation to cover the special problem of transportation of irradiated fuel elements (Title 10 of the *Code of Federal Regulations*, Part 72). A new proposed regulation has now been prepared (1) in the light of comments received, (2) in the light of further study by the AEC staff, and (3) following an Industry Advisory Conference held May 22, 1961, at which additional comments were received. The criteria and procedures apply to solid irradiated fuel elements containing 2000 or more curies of radioactivity in a single shipment. Smaller shipments may be made under existing federal regulations.

Casks in which spent fuel elements are shipped must be designed to maintain their structural integrity under all conditions of shipment and under conditions of severe impact since they must confine very high radiation intensities and high heat output generated by radioactive decay. In addition, any conditions of nuclear criticality must be prevented. Each licensee will be required to obtain AEC approval of cask design and shipping procedures. Because of special problems of different possible accident conditions and practical limits imposed by the excessive weights involved, shipment by air is not authorized in the proposed regulation.

Major changes that have been made in the proposed regulation since it was first published for public comment in March 1960 include:

1. Revision of the heat-transfer section to ensure that under emergency conditions fuel elements will not reach a temperature at which hazardous quantities of fission products would be released to the cask and possibly to the environment

2. Modification of the structural integrity criteria, which were originally based on a 30-ft drop test, to those based on a 15-ft free fall with a specific force that can be applied to satisfy the impact test. The additions of puncture and fire resistance, pressure design, lid hold-down requirements, and the beam type of static load test are believed to provide safety equal to that of the previously proposed regulation.

3. Permitting the use of mechanical cooling devices and of shipment under pressure up to 50 psig

4. A measure of the neutron multiplication which can be used to determine the degree of nuclear safety

5. Several additions as to compatibility of materials, contamination limits, and canning of ruptured fuel elements

Pending final adoption of the proposed regulation, the Commission will apply the criteria in the proposed rule in its review of applications for license to transport solid irradiated fuel elements.[4]

A shielded container for transporting radioactive spent fuel, designed at Knolls Atomic Power Laboratory (KAPL), has been described by Biggs.[5] This cask will be used in the movement of spent fuel across the country in depressed-center railroad cars. The unit will be 13 ft high and 7 ft in diameter and will weigh 250,000 lb. At the time of loading, the spent fuel will produce as much as 275,000 Btu/hr of decay heat, but at the time of shipment (approximately 30 days after loading) the decay heat will be reduced to about 75,000 Btu/hr. The container is cooled by water circulating through an internal heat exchanger, from which the heat is transferred to a secondary system coolant and dissipated by an air-cooled heat exchanger outside the container. For emergency, in the event of loss of coolant, heat is dissipated by a system of internal and external metal fins. To reduce the radiation dose rate to within the current requirements for Class D radioactive cargo, 11.5-in.-thick container walls of lead shielding are required. Rail cars are currently available to accommodate the container.

Fuel-Processing Costs

No commercial plants exist today for the processing of power fuels. In an effort to develop atomic power generation, the AEC has

contracted to process the irradiated power fuel elements and at the same time is attempting to interest private industry in radiochemical processing.

One of the questions facing the nuclear industry today is: When can private industry enter the spent-fuel-processing business with processing costs that the reactor operator can afford to pay? An economic analysis has been prepared by Guthrie at Oak Ridge National Laboratory (ORNL) in an attempt to answer this question.[6] In this analysis an attempt is made to estimate the amount that the reactor operator can afford to pay for processing fuel in a nuclear power industry in which the power costs are equal to the current average cost for electricity in the United States (6.8 mills/kw-hr). The author arrives at a cost of 0.35 mill/kw-hr as a reasonable radiochemical processing cost for competitive nuclear power. On the basis of reported cost estimates made independently by six different estimators for different processes, Guthrie then estimates that, in order to process spent fuels for 0.35 mill/kw-hr (at 8000 Mwd/ton burnup), a 6 ton/day plant operating at capacity would be required. This would require an installed nuclear capacity of 48,000 Mw (heat). From published nuclear power growth predictions, the 48,000-Mw nuclear capacity should be available about 1970, if the McKinney growth curve[7] is used.

The processing-plant installation capacity and the processing charges that can be envisioned (assuming that private processing plants are built, starting in 1962, to match the power-reactor fuel load) are shown in Fig. I-1. The upper curve shows the processing charges. Because of the small load, high processing costs result during the early years. Processing costs of 0.35 mill/kw-hr would be realized by about 1972.

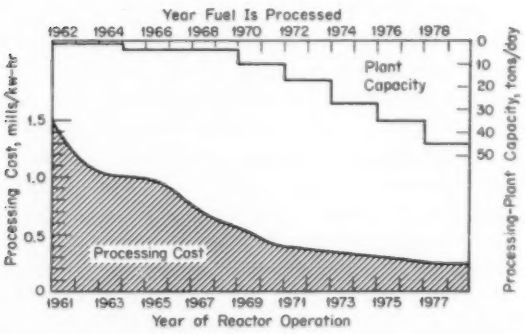
Year Fuel Is Processed
1962 1964 1966 1968 1970 1972 1974 1976 1978
Plant Capacity
Processing Cost
Processing Cost, mills/kw-hr
Processing-Plant Capacity, tons/day
0 0.5 1.0 1.5
0 10 20 30 40 50
1961 1963 1965 1967 1969 1971 1973 1975 1977
Year of Reactor Operation

Fig. I-1 Power-reactor fuel-processing costs and plant capacity—no stockpiling.[6]

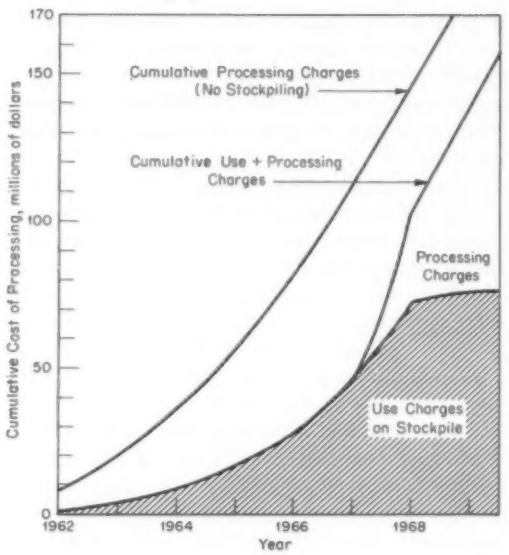
Cumulative Processing Charges (No Stockpiling)
Cumulative Use + Processing Charges
Processing Charges
Use Charges on Stockpile
Cumulative Cost of Processing, millions of dollars
0 50 100 150 170
1962 1964 1966 1968
Year

Fig. I-2 Effect of stockpiling on cumulative cost of processing fuel.[6] Basis: 2 per cent enriched fuel burned to 8000 Mwd/ton, average McKinney buildup curve, and 25 per cent thermal efficiency.

Guthrie points out that this 0.35 mill/kw-hr processing cost could be realized sooner (in 1967) if spent fuel from the whole industry were stockpiled in the early years. In this case the early costs are much higher than in the previous case because of the use charge on stockpiled material; however, the later costs are lower because large plants are built at an earlier date. If one looks at the total outlay required for processing and spent-fuel stockpiling (Fig. I-2), one can see that there may be an advantage to the industry as a whole to stockpile fuel in the early years. To be successful, this would have to be an industry-wide or government-sponsored program.

The AEC's interim processing program guarantees processing costs through June 1967. Stockpiling from 1967 instead of 1962 would delay the date at which a plant could be built by approximately one year (the amount of fuel discharged in the early years is small). The interim processing program thus reduces the cost

of processing without appreciably delaying the date at which private enterprise can enter the business with reasonable costs. This analysis, however, does not take into account the relative economics of future expansion of existing government-owned plants as opposed to construction of new ones.

The burnup attained in the reactors will also affect the economics. At twice the burnup, only half as much fuel has to be processed per unit of electricity. The processing costs are not cut in half, however, since with less fuel processed the unit cost is higher. Guthrie indicates that, by increasing the burnup from 8000 to 12,000 Mwd/ton, processing costs of 0.35 mill/kw-hr would be obtained in 1968 instead of 1970.

The cost estimates available at the time of Guthrie's analysis were prepared by various groups using different bases and estimating techniques. Most of these deal with only a single type of plant, and many of them were prepared at a time when relatively little experience and few data were available from production plants (as contrasted to pilot plants). Specifically lacking were data for independent, self-contained facilities and those which use mixer-settlers as the primary solvent-extraction-system contactors. Farrow,[8] at Savannah River, has recently reported the results of a study made at AEC request to provide design and cost data for modern separations plants that use mixer-settlers, based on Du Pont operating experience in the separations plant at Savannah River and that from other similar AEC operations.

Cost estimates and other information are provided for the following six specific cases:

Case I, a remote maintenance plant to process 10 tons of aluminum-clad natural uranium per day

Case II, same as Case I but using contact maintenance

Case III, same as Case I but for 1 ton/day

Cases IV, V, and VI, same as Case I except fuel to be clad with zirconium plus stainless steel or with either of these materials

It was assumed that the products of the plants were to be uranyl and plutonium nitrate solutions. The capital and direct operating cost estimates for six specific combinations of plant capacity, fuel enrichment, fuel cladding material, and maintenance methods are shown in Table I-1. The increased capital costs for Case II are the result of the dual equipment installed in the highly active parts of the process to ensure the required operating continuity. Operating costs are similarly increased due to the larger maintenance forces necessary when doing contact type work, the increased chemical consumption for decontamination prior to maintenance, and the additional costs of maintenance material.

The decreased capital cost for Case III is primarily the result of smaller canyon and

Table I-1 ESTIMATED CAPITAL AND DIRECT ADDITIONAL OPERATING COSTS FOR FUEL-PROCESSING PLANTS[8]

Case	Capacity, tons of U per day	Fuel enrichment	Fuel cladding	Maintenance method	Capital cost*	Annual direct operating cost*
I	10	Natural	Aluminum	Remote	60	6.2
II	10	Natural	Aluminum	Direct	70	6.4
III	1	Natural	Aluminum	Remote	65	3.7
IV		<5% U^{235}	Aluminum, Zircaloy, or zirconium	Remote	65	
V		<5% U^{235}	Aluminum or 300-series stainless steel	Remote	66	
VI		<5% U^{235}	Aluminum, zirconium, Zircaloy, or 300-series stainless steel	Remote	69	

*Millions of dollars.

auxiliary equipment. The capital costs are not reduced in proportion to plant capacity because of the relatively fixed costs for such items as the laboratory, administration building, shops, warehouses, distribution of utilities, and improvements to the areas. In many instances the cost of process equipment is similarly not proportional to capacity because of such things as remote canyon connections to process vessels where the number and therefore the cost of the connections stay the same regardless of plant capacity.

The increased capital costs associated with Cases IV, V, and VI are the result of additional process equipment, canyon building volume, and waste tankage, plus the use of more expensive alloy materials for the fuel-element dissolvers.

No finite capacity could be stated for the plants processing a variety of enriched elements, since the throughput rate will depend on the degree of enrichment, the complexity of disassembling and dissolving a specific fuel element, and the time required to flush and make the necessary changes when the process is shifted from one type of element to another. Similarly, the operating costs for these plants could not be estimated directly but would be of the same general magnitude as for the 10 ton/day remotely maintained plant.

Since the last three cases to be studied presume a plant to handle uranium containing both natural and low enrichment (under 5 per cent U^{235}), and since relatively large equipment is required to handle 10 tons of natural uranium per day, the equipment cannot be designed to be "geometrically safe." Concentration control is therefore the logical method for assuring nuclear safety, and it has been assumed that U^{235} concentrations must be maintained below 5 g/liter in order to give a sufficient margin of safety.

By assuming that the U^{235} concentration in the feed is maintained at 4 g/liter, the uranium and plutonium solvent-extraction capacities have been estimated (Table I-2). These are not necessarily plant capacities since these may well be limited by other parts of the process.

If one compares Farrow's estimates with the averaged cost data used by Guthrie for his analysis, one notes substantial differences. In general, it appears that Farrow's costs are considerably lower than Guthrie's for large-capacity natural-uranium plants and much higher in investment cost for small plants. This emphasizes further the advantage of large plants for lower processing costs. Guthrie assumed that natural and slightly enriched uranium could be processed at the same rate. The information in Table I-2 indicates that, in the case of Farrow's hypothetical plants, the capacity is appreciably reduced with increasing enrichment. Only at enrichments somewhat below 2 per cent, depending on the amount of burnup, would the plant capacity be substantially the same as for natural uranium.

Table I-2 ESTIMATED SOLVENT-EXTRACTION CAPACITY OF FUEL-PROCESSING PLANTS[8]

% U^{235} in unburned fuel	Exposure, Mwd/ton	Uranium, tons/day	Plutonium, kg/day	Equivalent reactor power, Mw(t)
Natural	1,000	10	10	10,000
Natural	5,000	10	38	50,000
5	5,000	2.6	1.8	13,000
5	25,000	5.4	18.4	135,000
25	11,000	0.5	1.9	5,000
93	200,000	0.2		36,000

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Aqueous processes for separating valuable products from used nuclear fuels were the first means developed for this purpose and are as yet the only plant-scale processes operated in the United States and the United Kingdom. Typical operations involve dissolving in acids and extracting and separating uranium and plutonium with organic solvents, although precipitation methods have been applied to effect separation and purification, and ion-exchange methods have been developed. New and more complex fuels require process modifications, and experience dictates the need for process improvements.

Preparation for Fuel Processing

Some complex nuclear fuels may require mechanical preparation to remove components with which it is undesirable or hazardous to burden the chemical process. Breaking up the elements mechanically may simplify the processing of other fuels. Further preparation for solvent extraction or other separating means, then, usually involves dissolving at least the fertile and fissionable material in acids.

Mechanical Processing Methods

In its annual progress report,[1] the ORNL Chemical Technology Division reports both on its experience with mechanical pretreatment of Sodium Reactor Experiment (SRE) fuel and on the operation of a 250-ton hydraulic shear.

The SRE dejacketing facility[2] has been used to prepare 1.8 tons of SRE core 1 fuel (25 clusters). It was reported that the equipment complex, consisting of a traversing-receiving table, multipurpose disassembly saw, hydraulic wire cutter, hydraulic dejacketer, slug steam cleaner, canning device, auxiliary dejacketer, and NaK disposal system, performed mechanically as expected. Operational bottlenecks were (1) transfer of canned fuel to a storage cell, (2) insertion of a canister containing a spent cluster from the carrier to the segmenting cell, (3) transfer of the NaK to a metering pot when the NaK was in an oxidized, waxy form, and (4) removal of jackets from highly pitted slugs after jacket cutting. Two minor NaK fires were experienced.

The fuel (burned to ~675 Mwd/ton and cooled ~2 years) had a much more brittle stainless-steel jacket (10 mils thick) than expected. The jacket was difficult to expand for removal even with hydraulic pressure up to 1700 psi. The slugs themselves were slightly bent and swollen 10 to 30 mils in diameter. The distortion and embrittlement resulted in a dejacketing rate of about 3 kg/hr versus the expected rate of 10 to 20 kg/hr.

In processing a typical cluster (70 kg), consisting of seven fuel rods, the following techniques were required. The slugs from one rod were removed hydraulically, and five rods required the use of a jackscrew ramrod to dislodge the slugs from the opened tubular jacket. The seventh rod was cut into 6-in. slug lengths, and these slug lengths were dejacketed separately in the auxiliary dejacketer. This dejacketer split the jackets by roller cutters, and the jackets were then pried from the slug surface.

The dejacketed slugs were canned in aluminum for processing after steaming off the NaK. The jackets were cleaned, flattened, and combined with other cluster parts for disposal by burial.

It was reported that dejacketing under an oil (Bayol-D) blanket worked well from a safety angle. Bayol-D is a deodorized, highly refined kerosene with a flash point of 185°F and con-

sists of highly branched saturated hydrocarbons containing a small amount of cyclic saturated hydrocarbons.

A 250-ton shear (fabricated by Birdsboro Corporation) was completed, and preparations were being made for tests on simulated multitube fuel assemblies (porcelain clad with stainless steel). Wear tests indicated that Stoody-1 [an alloy consisting of (weight per cent) 25 Cr, 13 W, 2 C, balance Co] was the best material for gibs and liners and that a water suspension of molybdenum disulfide greatly decreased the wear rate on liners. From tests on the one-fourth scale wooden model, it was reported that two-spray nozzles with a total capacity of 9.5 gal/min at 40 psi should be adequate to wash and decontaminate the inside of the full-sized shear. It is proposed that this shear be operated in conjunction with an inclined-drum nitric acid leaching device that will dissolve uranium dioxide fuel.

An interesting conceptual design for fuel-assembly sawing and fuel-pin chopping is reported in this section under the heading "Plant Design and Operation."

Chemical Removal of Stainless-Steel Jackets

Ferris and Kibbey[3] at ORNL have extended previously discussed work[2] on the chemical removal of type 316 stainless-steel jackets from the urania-thoria fuel pellets used in the Consolidated Edison (Indian Point) reactor. Since the urania content of the reactor fuel will vary from 3 to 10 per cent, the effect of variations in this factor on uranium and thorium losses to decladding solutions during treatment with 5*M* nitric acid–2*M* hydrochloric acid (Darex process) and with 6*M* sulfuric acid (Sulfex process) was determined. For a 48-hr exposure to boiling nitric-hydrochloric acid solution, losses of uranium increased from a few tenths to about 1 per cent as the urania content was increased from 3 to 9 per cent; losses of thorium were considerably lower but increased slightly. Losses of both elements to sulfuric acid were lower and showed less increase with increasing urania content. Correlations were developed for the density (at 26°C) of the stainless-steel sulfate solutions as functions of sulfuric acid and dissolved stainless-steel concentrations, and considerable data are reported for factors affecting the rate of dissolution of urania-thoria pellets in concentrated nitric acid containing 0.04*M* fluoride.

Oak Ridge concludes that uranium losses to the nitric-hydrochloric acid mixture are too high for this to be applicable for decladding stainless-steel-jacketed thoria-urania pellets.[1] Losses from prototype Consolidated Edison fuel pins treated 1 hr with the nitric-hydrochloric reagent increased from 0.04 per cent for unirradiated pins to 3 per cent for pins irradiated to 25,000 Mwd/ton of fuel. Losses increased with exposed oxide surface area, and many pellets were fragmented when irradiated to burnups greater than 500 Mwd/ton. In contrast to experience with nitric-hydrochloric acid reagent, uranium losses from treatment with 4*M* to 6*M* sulfuric acid were low (generally less than 0.4 per cent) and not greatly affected by extent of irradiation.

Metallic fuel elements that utilize a reactive liquid-metal bond (Na or NaK) to stainless-steel jackets constitute a difficult processing problem. When the jacket is penetrated and the bond material is exposed, it may react violently with water or aqueous reagents. At ORNL, Adams has surveyed the hazards of processing such materials[4] and has concluded that aqua regia and sulfuric acid decladding processes do not appear to be feasible for processing such fuel types. Nitric-hydrochloric acid decladding is regarded as prohibitively hazardous, as nitrogen oxide–hydrogen explosions appear unavoidable. Direct sulfuric acid decladding, or decladding after reaction of the sodium bond, was thought to be less hazardous and possibly feasible. For small fuel elements containing only few-gram amounts of sodium, it was conceived that destruction of the sodium could probably be accomplished safely by shearing rods or bundles into short lengths and reacting *in situ* with water.

Total Dissolution of Metallic Fuel Materials

Dissolution of Uranium and Uranium Alloys. Unalloyed uranium rods have been frequently used as fuels for plutonium-producing reactors, but relatively little work has been reported on their dissolution characteristics. Lacher et al. have recently reported work on the influence of various factors on the dissolution rate of relatively pure uranium metal.[5] It was found, for example, that the dissolution rate in nitric acid depended on the presence of impurities and on

metallurgical treatment. Samples containing 350 to 560 ppm carbon and 43 to 109 ppm nitrogen dissolved in concentrated nitric acid at 0°C at initial rates of 0.50 to 0.83 mg/(cm²)(hr), whereas samples containing 15 to 35 ppm carbon and 9 to 26 ppm nitrogen dissolved at initial rates of only 0.11 to 0.26 mg/(cm²)(hr). Rolling of the metal appeared to result in preferential attack along the axis. Addition of potassium nitrite to 6*M* acid enhanced the dissolution rate markedly but was less effective in concentrated acid, whereas addition of urea (a nitrite-destroyer) inhibited attack. It was also observed that agitation of the solution reduced the dissolution rate, presumably due to the removal of nitrous acid catalyst. At both 0 and 25°C, the rate of attack increased rapidly (greater than a fifth-power dependence) with increasing acid concentration up to about 12*M*.

In a summary of studies on preparation of feeds suitable for tributyl phosphate (TBP) extraction from uranium-molybdenum alloys, Ferris at ORNL[6] has recommended the dissolving of 3 per cent molybdenum alloy (as found in the Enrico Fermi reactor blanket) in 6*M* nitric acid and of 10 per cent molybdenum alloy (fuel used in the Consumers Public Power District reactor, Hallam, Nebr.) in 11*M* nitric acid. Flow sheets for these processes are shown in Figs. II-1 and II-2. Because of the hazard involved in reacting sodium with mineral acids, it was assumed that both the cladding and sodium bond would be removed mechanically and that the fuel would be recanned in aluminum before processing. A stable feed solution that contains all the molybdenum in solution is thus prepared from the 3 per cent alloy, but the 10 per cent alloy yields a bulky molybdic oxide precipitate that carries 5 to 10 per cent of the uranium. The latter is recovered by dissolving the molybdic acid in caustic, removing the solution, and dissolving the residual uranium precipitate in nitric acid for addition to the feed. For the 3 per cent molybdenum alloy, an alternative process involving dissolution in 8*M* nitric acid containing 0.5*M* ferric nitrate is also

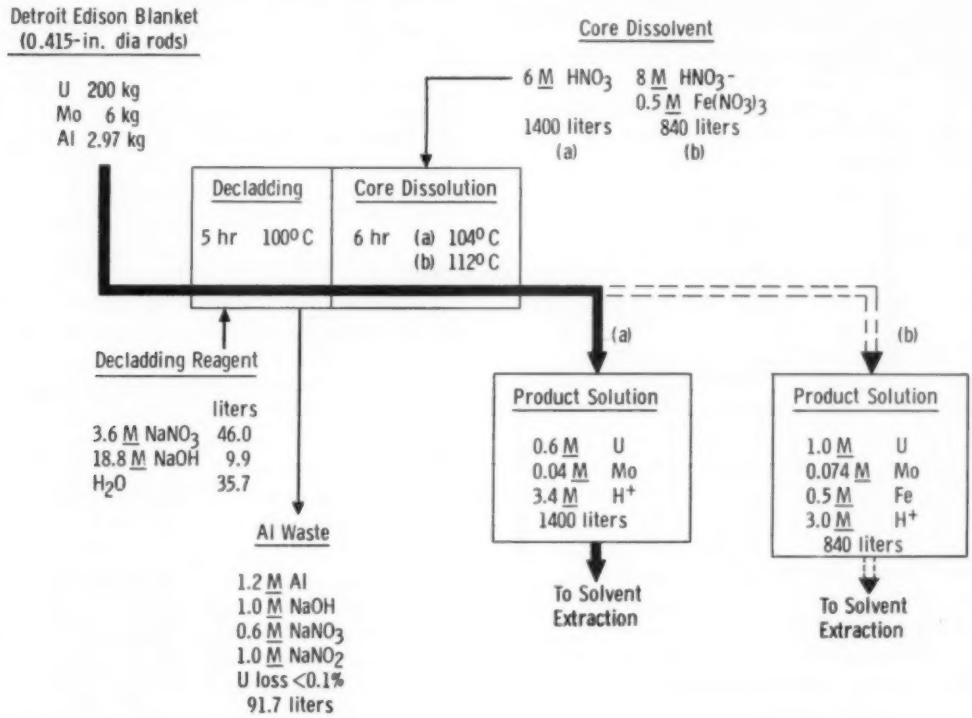

Fig. II-1 Processes for dissolution of uranium–3 per cent molybdenum alloy fuels.[6]

shown. Feed volume is thereby reduced 40 per cent, but concentration of the waste is limited by the iron content.

Dissolution rates for 3 and 10 per cent molybdenum alloys are greater than for unalloyed uranium and generally exceed 10 mg/(cm^2)(hr). If the terminal acidity in dissolving 3 per cent molybdenum alloy is carried to 1.25*N*, a uranium-bearing solid is formed. This occurs with the 10 per cent alloy at terminal acidities of 3.2*N* or lower and is apparently due to the formation of uranyl molybdates of undefined composition. Dissolution in nitric acid–phosphoric acid mixtures was also explored. Dissolution is rapid in 8*N* to 10*N* nitric acid containing 0.25*M* to 10*M* phosphoric acid and is slowed considerably in 3*N* nitric acid. The solubility of molybdic oxide is adequate to provide stable solution in 3*N* acid with phosphoric acid concentrations approaching 1*M*, but decreases with increasing acidity, and might be inadequate to prepare alloy solutions from 8*N* to 10*N* nitric acid. Phosphoric acid at useful concentrations is of questionable interest for preparing molybdenum alloy solutions, since the addition of a corresponding concentration of an iron salt would be necessary to permit complete uranium extraction from such solutions. Extensive solubility data for hydrated and unhydrated molybdic oxide in nitric acid containing ferric and uranyl nitrates were also reported by Ferris.[7]

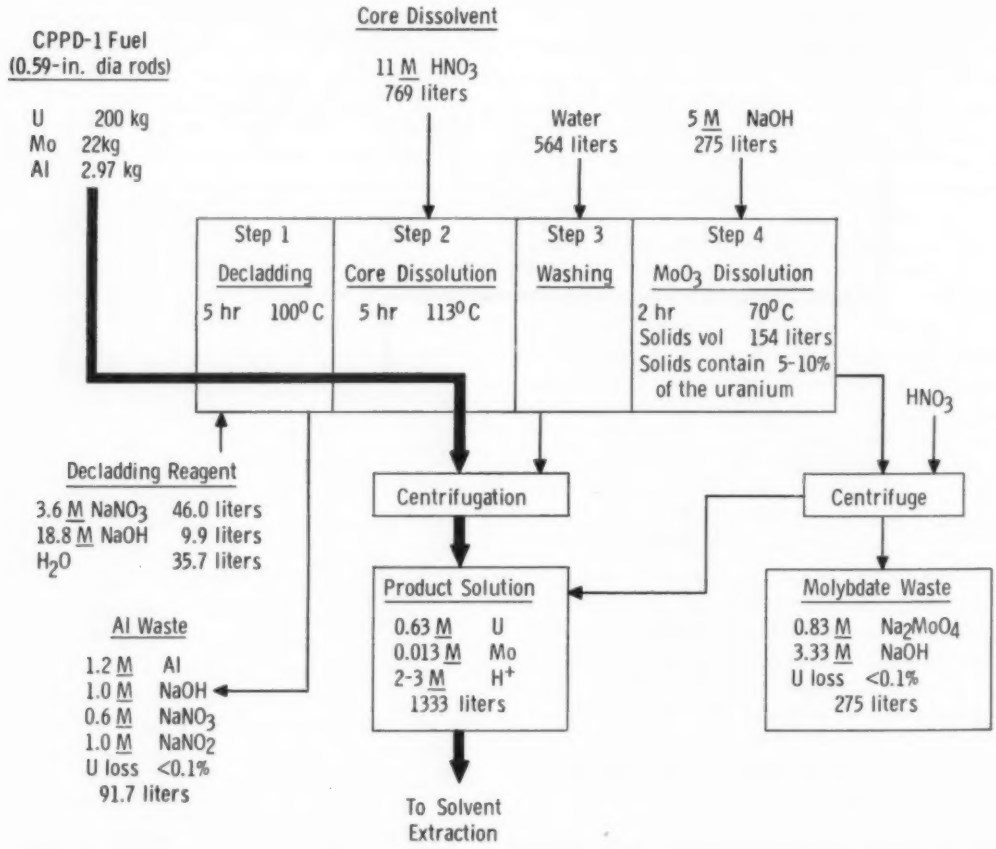

Fig. II-2 Process for dissolution of uranium–10 per cent molybdenum alloy fuel.[6]

Dissolution of Zirconium-Rich Fuels. Zirconium-rich fuels, which are typically an alloy of zirconium with a few per cent of rather highly enriched uranium, and which may be Zircaloy

clad, are presently processed by dissolving in hydrofluoric acid or ammonium fluoride with the addition of peroxide or nitrate ion to obtain complete solution. At Oak Ridge, consideration has been given to other dissolving reagents that would be compatible with a titanium dissolver vessel; this same vessel would be used for dissolving other fuels in nitric and nitric-hydrochloric acid mixtures.[8] The most promising reagent found is concentrated nitric acid containing a small amount of fluoboric acid, at least 1.4*M* zirconium, and about 2.6*M* fluoride. Although dissolution and corrosion rates decreased with increasing zirconium concentration, the dissolution rate at 1.47*M* zirconium was acceptable at a value of 2.8 mg/(cm^2)(min). The raw product solution was stable hot, cold, and diluted with water.

Robson et al. at Harwell have described a modification of the hydrofluoric acid process for zirconium which was initially developed for recovery of uranium from alloy scrap.[9] The alloy is largely dissolved in 10*M* hydrofluoric acid containing a small quantity of potassium fluoride. A complex fluoride precipitate is formed which contains substantially all the uranium. After filtering away from the dissolver solution, the fluoride precipitate is washed with a small volume of dilute potassium fluoride and is dissolved in an aluminum nitrate–nitric acid solution, containing sufficient dichromate to oxidize uranium to the hexavalent state, to yield an extraction-process feed solution much like that obtained in the hydrofluoric acid process. From Zircaloy-2 containing 5 per cent uranium, 99.8 per cent of the uranium was recovered in the feed solution. In tests with highly irradiated fuel alloy, cesium and niobium were found in the dissolver filtrate, whereas most of the strontium, ruthenium, and rare earths accompanied the uranium. Claimed advantages of the process include preliminary separation of zirconium from the alloy and a low volume of extraction-process waste. However, waste from both the dissolving and extraction steps will be radioactive.

A patent has been issued[10] to Gens of ORNL covering the addition of peroxide to ammonium fluoride in dissolving zirconium-uranium alloys, in order to retain greater amounts of uranium in solution than are retained when uranium tetrafluoride is dissolved in ammonium fluoride. This pertains to what is called the Perflex process.

Dissolving Stainless-Steel Fuels. Several experimental and test reactors—the Stationary Medium Power Plant No. 1 (SM-1) [formerly called the Army Package Power Reactor (APPR)], the General Electric Test Reactor (GETR), and the Organic-Moderated Reactor Experiment (OMRE)—utilize a plate type highly enriched uranium fuel composed of a layer of uranium dioxide dispersed in stainless steel (prepared by powder-metallurgy techniques) which is clad with stainless steel. The Experimental Organic-Cooled Reactor (EOCR) will also use such a fuel for its driver elements. Fuels of this type can be processed by a means developed at KAPL for the Submarine Intermediate Reactor (SIR) fuel.[11] The process involves dissolving the stainless steel in 6*M* sulfuric acid, adding nitric acid to the solution to dissolve the uranium dioxide, and extracting the uranium with a TBP-diluent mixture.

Recovery of uranium from the first OMRE core by such a process at the ICPP was recently reported by Ayers and Raab.[12] An unusual problem was provided by the exposure of the fuel to the organic coolant (a mixture of polyphenyl compounds) in the reactor. The fuel elements had become coated with a thin film composed of a carbonaceous degradation product of the reactor coolant together with some inorganic material. It was necessary to remove this film before processing so that sulfuric acid could attack the stainless-steel cladding.

Tests on coupons cut from a fully irradiated fuel element indicated that this coating was resistant to boiling concentrated sulfuric acid, 8*M* sodium hydroxide, 1*M* hydrogen peroxide with or without 6*M* sulfuric acid, and many of the more common organic solvents. The film was attacked, however, by a hot commercial caustic-permanganate decontaminating and cleaning reagent (Turco 4502), or by heating the element in air at 500°C. The Turco treatment was selected for plant operation since its use would require no plant modification if the film removal step were carried out in the dissolver. Treatment consisted of immersing the elements in a boiling solution containing 2 lb of the Turco 4502 reagent per gallon, followed by washing with water before sulfuric acid dissolution.

Coating removal appeared to be successful, since dissolving progressed satisfactorily. Capacity of the dissolving equipment was markedly reduced, however, by the time necessary for the pretreatment, as well as by the large size

of the element which necessitated attacking it twice with sulfuric and nitric acids. Some difficulty experienced in jetting solutions may have been due to clogging of orifices and lines with particles of the organic deposit. Uranium losses were small, and decontamination was adequate.

At the ICPP, consideration is now being given to processing a second OMRE core, the elements of which possess a similar deposit. The coating on one core-2 sample was easily removed by scraping with a Lucite scraper operated by a master-slave manipulator.[13] Turco 4502 was again effective in removing the coating.[14] Filtration of the used coating-removal solution left a residue that contained an iron carbide, and manganese contaminated with cerium and zirconium, whereas the filtrate contained cesium and very little iron.

Treatment of Nonmetallic Fuels

Since increasingly higher operating temperatures are required in reactor fuels, a variety of nonmetallic fuel materials have become of interest. These are chiefly of a ceramic nature and include graphite bodies, carbides, and high-temperature stable oxides such as beryllia, alumina, and urania. Processing such materials to recover fissionable material presents unusual problems due to their generally chemically refractory nature.

Graphite Bodies. Fuel for the Turret reactor being developed at Los Alamos is produced simply by impregnating graphite with uranyl nitrate solution and baking to decompose the salt. Oak Ridge has reported that leaching such a material twice with boiling nitric acid results in a loss of only 0.012 per cent of the uranium to the residue[15] and that the uranium loss was only 0.09 per cent when leaching[8] was conducted at 25°C. Good results were also obtained by applying repeated leaching with boiling 90 per cent nitric acid to a graphite specimen containing 1.3 per cent uranium and 15 per cent thorium as uncoated carbide particles dispersed in a graphite matrix. Losses were only 0.01 per cent of the uranium and 0.16 per cent of the thorium.[16] However, when the same treatment was applied to a similar specimen containing higher concentrations of uranium and thorium as pyrolytic carbon-coated graphite particles, only about 5 per cent of the uranium and thorium was recovered. It is felt that the shell-like structure of pyrolytic coatings results in great resistance of the coatings to penetration by reagents.

Carbide Fuels. Carbides may yield hydrogen and hydrocarbon gases on reaction with aqueous reagents. Bradley and Ferris[17] have recently given details of their previously discussed[18] work on the hydrolysis of uranium carbides. Additional work at ORNL[1] has indicated that, as the carbon-to-uranium ratio in the carbide increased from 1 to 1.6, the hydrogen concentration in the off-gas increased from 10 to 23 per cent, whereas the methane concentration decreased from 87 to 14 per cent as shown in Table II-1. The total volume of gas evolved decreased from 93 to 32 ml/g as the carbon-to-uranium ratio increased. The samples that had a carbon-to-uranium ratio greater than 1 also yielded an unidentified brown waxy substance.

Beryllium Oxide Fuels. Mixtures of beryllium oxide and uranium dioxide are being considered for gas-cooled-reactor fuel elements. These are in two main categories: (1) those containing more than 60 wt.% uranium dioxide, e.g., those planned for the Gas-Cooled Reactor

Table II-1 REACTION OF URANIUM CARBIDES WITH WATER[1] AT 80°C

(Helium Atmosphere; Analysis by Gas Chromatography)

Carbide composition								
	Millimoles/g							
C/U mole ratio	U	Combined C	Total gas volume (STP), ml/g	Total volatile carbon, millimoles/g	Av. gas composition, vol.% H_2	CH_4	C_2H_6	C_3 to C_5
0.99	3.99	3.95	93.0	3.91	10.4	86.7	1.8	1.07
1.06	3.99	4.22	85.3	3.62*	12.5	81.1	5.4	*
1.20	3.93	4.71	76.6	3.40*	13.8	75.2	8.2	*
1.63†	3.81	6.22†	31.7	3.1	23	14	38	22

*Analytical procedure not very sensitive for higher hydrocarbons.

†Assuming that free carbon left after hydrolysis was unreacted in original specimen.

Experiment (GCRE) and the Maritime Gas-Cooled Reactor (MGCR) and (2) those containing less than 10 wt.% uranium dioxide. The ceramic material generally is in the form of small pellets and may be clad in a metal alloy such as Hastelloy X. Uranium may be recovered[18,19] from the high urania pellets at varying rates by leaching with or dissolving in 6*M* to 13*M* nitric acid, ammonium bifluoride solution, nitric-sulfuric acid mixtures, and certain nitric-hydrochloric acid mixtures. The latter also dissolve Hastelloy X.

Oak Ridge workers report that materials containing less than 10 per cent uranium dioxide do not dissolve rapidly in common aqueous reagents.[1] Tests were made with sintered beryllia and with sintered beryllia–5 and –8 per cent uranium dioxide pellets. Rates were less than 0.3 mg/(cm^2)(min) in 4*M* to 16*M* nitric acid, 4*M* to 8*M* sulfuric acid, and 3*M* to 8*M* ammonium fluoride. Ammonium bifluoride solution, with and without ammonium nitrate, effected dissolution at rates of the order of 2 mg/(cm^2)(min). In later work, 15*M* sulfuric acid,[16] and up to 5*M* fluoboric acid in 5*M* to 15*M* hydrofluoric acid,[8] were found to dissolve 5 per cent uranium dioxide pellets with reasonable speed [0.7 to 3 mg/(cm^2)(min)]. Fluoboric acid alone effected much slower dissolution.

Solvent-Extraction Processes

Extraction of uranium, plutonium, and thorium from aqueous solutions with organic solvents continues to be the principal means for recovering and purifying these elements. Principal areas for current research exist in the fields of radiation and chemical stability of solvents, mechanisms for their degradation, and investigation of potentially useful new solvents.

Extraction-Process Modifications

At Oak Ridge a significant modification of the TBP process for recovery of thorium and U^{233} from irradiated thorium has been developed.[1] An older process has been known as the Thorex process. In the new acid Thorex process, nitric acid rather than aluminum nitrate is used to increase the salting strength of the feed solution. This permits markedly greater concentration of the process waste. Uranium and thorium are simultaneously extracted from an acid-deficient feed stream with 30 per cent TBP in a hydrocarbon diluent. The salting acid is added below the feed point. After nitric acid and water scrubbing of the loaded solvent, it is fed to a partitioning column. Thorium is stripped with 0.01*M* nitric acid, and uranium is scrubbed from the aqueous stream with fresh solvent. Uranium is finally stripped from the solvent in a third column into 0.01*M* nitric acid.

This flow sheet was demonstrated in 2-in.-diameter pulse columns. Losses of both uranium and thorium were less than 0.1 per cent. Revision of the process so that part of the aqueous stream from the uranium stripping column was returned as a stripping agent for thorium permitted concentration of the uranium product stream to 20 g/liter with continued low losses. Flow capacity and efficiency of both sieve and nozzle plate columns corresponded to similar data for a standard Purex flow sheet.

In decontamination studies in miniature mixer-settler equipment, decontamination factors of 10^4, 5×10^3, and 2×10^5 from ruthenium, zirconium-niobium, and rare earths were obtained. The limiting activity in each product was zirconium-niobium.

The use of dibasic aluminum nitrate to strip thorium selectively from the 30 per cent TBP thorium-uranium extract was also studied. This gave an acid-deficient thorium product solution which could be concentrated by evaporation to prepare feed for the succeeding cycle without the high-temperature feed adjustment required with dilute nitric acid stripping. Uranium product was also more concentrated as a result of less acid in the organic phase going to the stripping column. Flow-sheet conditions for the partition column were:

Stream	Relative volume	Composition
Feed	7.0	42 g of thorium per liter 2.7 g of uranium per liter 0.5*M* HNO_3 in 30% TBP in Amsco diluent
Strip	4.2	0.05*M* dibasic aluminum nitrate
Scrub	1.4	30% TBP in Amsco diluent

Coleman at Oak Ridge has described a possible modification of the Purex process in which final recovery and purification of plutonium is accomplished by extracting the partitioned plutonium with a tertiary amine rather than by

submitting it to one or more separate TBP extraction cycles plus concentration by ion exchange or evaporation.[20] This process is based on the fact that many tertiary amines are strong complexing agents for plutonium in the tetravalent state. Other heavy metals are similarly complexed and extracted, but effective separation can be made. To compete with TBP extraction and anion exchange, amine extraction must provide high decontamination and reasonably high concentration of the plutonium in a single cycle, as well as being simpler and consuming less acid. The currently visualized flow sheet shown in Fig II-3 will take as feed a Purex partition-cycle plutonium-product stream containing nitric acid in the range 1*M* to 2*M*, with some sulfate. The only feed adjustment necessary appears to be reoxidation with nitrite. It may be desirable to reduce TBP carry-over by diluent scrubbing.

With expected feed concentrations of 0.5 to 2 g of plutonium per liter, the desired product concentrations of 20 to 60 g/liter should be obtainable with an amine concentration of 0.3*M*. The extraction coefficients for tetravalent plutonium remain high enough over a wide nitric acid concentration range to permit scrubbing at either rather high or rather low acidity in order to emphasize eliminating either ruthenium or zirconium. No decontamination data are yet available.

Solvent Degradation and Treatment

At Oak Ridge a somewhat different test has been used to evaluate degradation of used TBP-diluent mixtures rather than the Z test used at the Savannah River Laboratory.[21] The Savannah River test consists of prewashing the solvent with caustic, water, and nitric acid and equilibrating this washed solvent with zirconium tracer solution. After scrubbing three times with 3*M* nitric acid to remove the bulk of the zirconium complexed by TBP, the retained zirconium is measured. The Oak Ridge test has included scrubbing the diluent beforehand with dilute sodium carbonate (to remove TBP hydrolysis products) and then measuring zirconium extracted on contact with a zirconium nitrate tracer solution. Oak Ridge has now modified its test to include contacting the carbonate-washed solvent with solid calcium hydroxide prior to determining zirconium extraction.[1] The purpose of this is to convert nitroparaffins formed by diluent degradation into the salt form, from which they are rapidly convertible to the enol or acid form which is effective in zirconium binding in the presence of TBP.

Figure II-4 shows the results of testing a 1*M* TBP solution in a hydrocarbon diluent which had been irradiated by a Co^{60} source while intimately mixed with 2*M* nitric acid. Carbonate scrubbing markedly decreased zirconium extraction from the irradiated solvent, but addi-

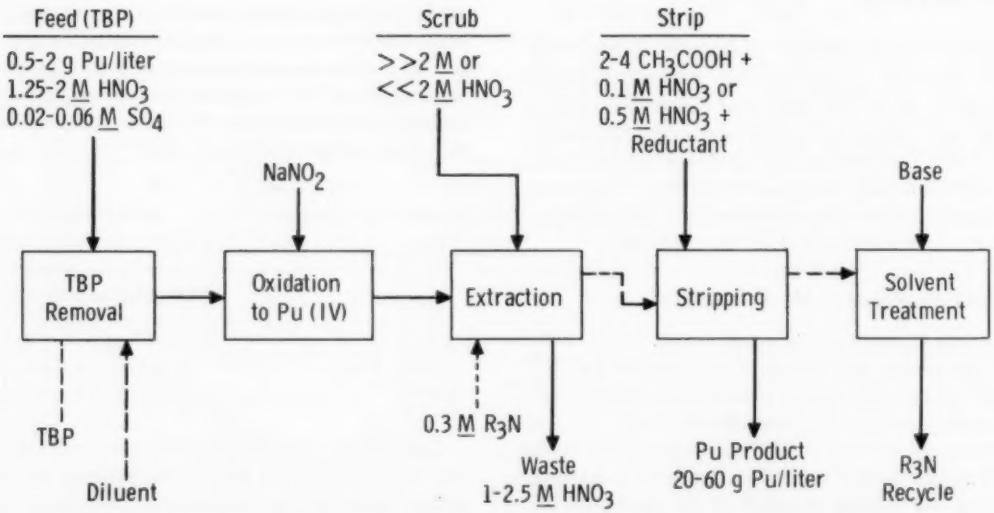

Fig. II-3 Amine extraction cycle for final plutonium recovery.[1]

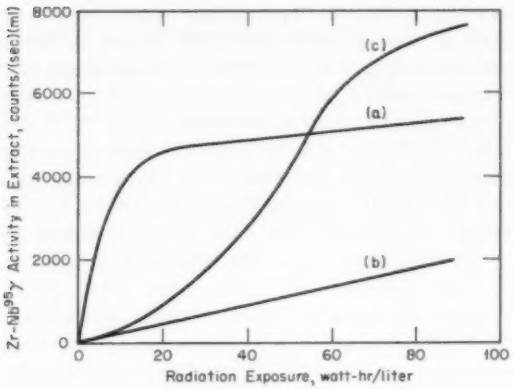

Fig. II-4 Extraction of Zr^{95}-Nb^{95} by degraded TBP.[1] (*a*) 1*M* TBP in Amsco 125-82 degraded by irradiation while in contact with aqueous nitric acid. (*b*) Degraded solvent scrubbed with aqueous sodium carbonate. (*c*) Degraded and scrubbed solvent treated with calcium hydroxide. Extraction from 2*M* HNO_3, containing initially Zr^{95}-Nb^{95} at 10^4 counts/(sec)(ml).

tional contact of the more highly irradiated solvent samples with calcium hydroxide resulted in greater zirconium extraction than occurred for material washed with carbonate alone.

At the Savannah River Laboratory, efforts have been made to determine the hydrocarbon types present in the Ultrasene diluent used there in plant operations, to separate the diluent into fractions according to hydrocarbon type, and to characterize the stability of the various classes of hydrocarbons found.[22] Fractionation was effected by isolating straight-chain paraffins as urea adducts, adsorbing aromatics on silica gel, and separating slightly branched paraffins from highly branched paraffins and cycloparaffins by thiourea treatment. Analyses were performed by gas chromatography, infrared spectrophotometry, and low-ionizing-voltage mass spectrometry.

The diluent appeared to be composed principally of normal, highly branched, and cyclic paraffins in the C_{11} to C_{16} range. A typical analysis was as follows:

Composition of Ultrasene[22]

Hydrocarbon type	Wt.%
Normal paraffins	40
Branched and cyclic paraffins	57
Aromatics	3
Olefins	<0.1

The aromatic compounds were principally alkylbenzenes and aromatic cycloparaffins. Three-fourths of the normal paraffin fraction was dodecane and tridecane.

Stability of the fractions in mixtures with 30 per cent TBP was evaluated, after subjecting to radiolytic or chemical degradation and caustic and acid washing, by subjecting to the Z test described above. The normal paraffins were most stable, whereas the branched and cycloparaffins and aromatics were significantly less stable, as indicated by tendencies to form zirconium ligands. However, removing aromatics from Ultrasene did not improve its stability.

At Hanford, work has continued on the evaluation of alternative Purex-process diluents. Solutions of 30 per cent TBP in Shell E2392, Shell 85030, Soltrol 170, and *n*-dodecane were subjected to four cycles of nitric-nitrous acid degradation and carbonate-permanganate washing. Following each degradation, a small part of each solvent was carried through a use test simulating the extraction, scrubbing, and stripping operations of the Purex process. Best results were obtained with dodecane. The ratios of retained zirconium-niobium activity for the Shell 2342, Shell 85030, Soltrol 170, and dodecane diluents were in the proportion 2300:320:25:1. Disengaging time after degradation was increased significantly for Shell 2342, was less for Shell 85030, and was not affected for Soltrol 170 and dodecane.[23]

At the Idaho Chemical Processing Plant (ICPP), difficulties in removing very small amounts of plutonium from used solvent have prompted the investigation of solvent cleanup by steam distillation. In this case the purpose of the treatment is only to permit disposal of the used solvent by incineration or drum storage. The ICPP processes include a step wherein first-cycle uranium product before concentration is washed with diluent to remove entrained TBP. The used wash diluent gradually accumulates some TBP and may be mixed with discarded solvent prior to disposal. Plutonium may be introduced in microgram quantities (which nevertheless represent an incineration hazard) as plutonium polymer or as monobutyl or dibutyl phosphate complexes.

Ford and Chamberlain,[24] in studying the treatment of such a stream on a pilot-plant scale, have concluded that neither activated carbon nor ferrous sulfamate treatment can as-

sure effective plutonium removal but that it is feasible to steam-distill 99 per cent of the waste solvent overhead through a short packed column (leaving a residue of only about 1 per cent which is largely TBP and contains the nonvolatile plutonium), using a steam-to-solvent ratio of about 4 and a column temperature of 300°F. It should be possible to process solvent containing up to at least 30 per cent TBP by these means. It appears feasible to use such a system to reclaim solvent for reuse, but no evaluation of the quality of the distilled solvent was made.

Empirical observations at Oak Ridge in the course of solvent-extraction process development some years ago indicated that treatment of process feed solutions with acetone and nitrous acid improved decontamination from ruthenium. Recently an explanation of such behavior has been postulated on the basis that nitrous acid and certain ketones will react to form ketoximes, and that such compounds are potentially strong complexing agents for metal ions such as ruthenium and zirconium. Blake and Schmitt at Oak Ridge have observed that a similar ketoxime, diacetylmonoxime (derived from methyl ethyl ketone) produces marked improvements in zirconium decontamination in laboratory tests, particularly when degraded solvent capable of complexing zirconium is employed.

Ion-Exchange Processes

Ion-exchange applications in the nuclear fuel-processing field are principally encountered in plutonium-product purification and concentration and in the recovery of special products such as transuranic materials and fission products. Discussion of the last topic will be found in Sec. IV, "Waste Disposal."

Mainland, in collaboration with Orth, Field, and Radke, has provided an excellent description of the cation-exchange process used for plutonium concentration at the Savannah River Plant.[25] The article describes equipment used and indicates typical process conditions and operating results and problems. The subsequent steps of plutonium peroxide precipitation and decomposition, hydrofluorination, and reduction are also described in detail.

The ion-exchange process used is essentially the same as one reported previously which was developed for the Oak Ridge metal-recovery plant.[26] The product from the Purex solvent-extraction process is a stream containing a low concentration (0.2 to 1.2 g/liter) of trivalent plutonium in nitrate solution (0.2*M* to 0.6*M* nitric acid) and 0.25*M* to 0.05*M* hydroxylamine sulfate. This is adsorbed onto Dowex 50W (50 to 100 mesh) ion-exchange resin contained either in a single bed 7 in. in diameter and 13 to 15.5 in. high or in two consecutive beds 10 in. in diameter and 5 in. high. Flow rates through the spring-loaded columns range from 10 to 20 ml/(min)(cm^2). The size of the batch adsorbed ranges from 350 to 850 g of plutonium, in addition to the column heel normally retained which is 5 to 15 per cent of the batch size. Residual uranium and minor amounts of fission-product contamination are removed from the resin by washing with 6 to 24 volume changes (one volume change is assumed equal to half of the physical volume of the bed) of 0.19*M* to 0.25*M* sulfuric acid containing 0.05*M* hydroxylamine sulfate. Plutonium is next eluted from the bed, by reverse flow with a stream of 5.7*M* nitric acid containing 0.3*M* sulfamic acid, at the much lower rate of 0.2 to 0.5 ml/(min)(cm^2) to give a purified plutonium stream at a concentration of 50 to 70 g of plutonium per liter. Less concentrated fore and tailings fractions are recycled. Finally the bed is prepared for reuse by slow passage of 2 volume changes of a reconditioning wash of 0.1*M* nitric acid containing 0.05*M* hydroxylamine sulfate.

Losses of plutonium in absorption and to the decontaminating wash can be held to the low level of 0.0001 per cent, but excessive amounts of elutriant and long time cycles are required as compared to operation at an acceptable loss level of 0.01 per cent. Since the feed composition varies somewhat, the volume of the sulfuric acid decontamination wash is set in a sliding scale according to the amounts of uranium and zirconium-niobium in the feed and the required decontamination. Concentration of the wash is a matter of choice; the 0.19*M* solution gives slightly poorer decontamination than the 0.25*M* solution, but losses are considerably lower. Approximate ranges in decontamination factors which have been obtained are shown in Table II-2.

Decontamination from zirconium and niobium is increased by sulfate complexing when the wash is used; without the wash it is a case of preferential elution of plutonium. Off-standard

Table II-2 DECONTAMINATION FACTORS FOR PLUTONIUM[25]

(Resin Wash Solution: 0.19*M* or 0.25*M* Sulfuric Acid with 0.05*M* Hydroxylamine Sulfate)

Volume changes of wash	Ru decontamination factor	Zr-Nb decontamination factor	Uranium decontamination factor	
			If U/Pu <0.1	If U/Pu >0.5
9	2–4	1–10	4–20	>20
24	2–4	10–70	30–80	>100

solvent-extraction operations apparently form an abnormal species of zirconium-niobium in the feed. This species is not readily removed and can reduce decontamination below the normal limit. The circumstances under which this is encountered indicate that it is formed by association with degraded organic material in the process solvent.

The composition of the nitric and sulfamic acid eluant is set by the solubility limit of sulfamic acid and the maximum acid concentration compatible with maintaining trivalent plutonium. Its volume, which varies from 1.6 to 4.0 volume changes, is based primarily on waste losses. With 50- to 100-mesh resin, there is little difference in elution characteristics below a rate of 0.2 ml/(min)(cm^2). As the rate is increased, the elution curve for plutonium begins to spread, and losses rapidly become greater at rates higher than 0.5 ml/(min)(cm^2).

Exact composition of the reconditioning wash solution is not important since it serves only to restore a dilute acid condition and to provide a hydroxylamine environment. After a shutdown period, a refrigerated wash of this type may be used to remove gas. Gas may be formed from radiolytic oxidation of plutonium on a loaded column or by reactions of the reducing agents. Limiting the peak concentration of the eluting solution to 130 g of plutonium per liter has permitted many months of operation without appreciable oxidation.

Occasionally, accumulated fission products on the column must be removed for maintenance or replacement of the unit. Oxalic acid solution (0.5*M*) has been very effective for this purpose. The plutonium heel is first removed with an extended product elution (10 volume changes). The volume of oxalic acid solution used depends on the decontamination required. Typically, 5 volume changes will reduce radiation by a factor of 20.

In another ion-exchange application,[27] Laggis and Schmitt at Y-12 propose to recover and purify neptunium present at only microgram levels from a dilute and slightly acidic uranyl nitrate solution. Tests were made with Dowex 50W resin (8 per cent cross-linked) on a uranium-bearing 0.34*N* nitric acid feed solution containing 1.1 μg of neptunium per liter to which 0.01*M* ferrous sulfamate was added. It appeared that over 99 per cent of the neptunium was retained by the resin after treatment of 1300 column volumes of influent. Uranium was first eluted with 1.0*M* nitric acid, with very little loss of neptunium, and the neptunium was then eluted practically quantitatively with either 1.25*M* sodium bisulfate or with 6*N* nitric acid. When a feed solution, which had been concentrated fivefold by evaporation (to about 0.1*M* uranyl nitrate) and adjusted to 0.3*N* acidity with ammonia, was passed through the resin column, little neptunium was adsorbed presumably because of the high uranium concentration.

Most of the small amount of ruthenium present, and a few per cent of the zirconium-niobium, accompanied the neptunium through the cation-exchange process. The neptunium eluted by 6*M* nitric acid was further purified by two cycles of anion-exchange treatment using Dowex 1 X-1 resin. Adsorption onto the resin was conducted from an 8*M* nitric acid stream containing 0.01*M* ferrous sulfamate. Uranium and fission products were eluted with 15 to 25 column volumes of 8*M* nitric acid, and the neptunium product was eluted with 0.3*M* nitric acid.

Process Instrumentation

An interesting solution to the ever-present problem of in-line density measurement in a pulse column is presented in an ORNL report.[28] Figure II-5 shows the basic design. The principle of operation is as follows: the position of the float changes as the density of the liquid changes because of the change in requirement of spring tension to balance the buoyant forces on the float. The differential transformer precisely measures the change in position of the float and provides a signal that, with proper electronic modification, can be measured on the Brown recorder.

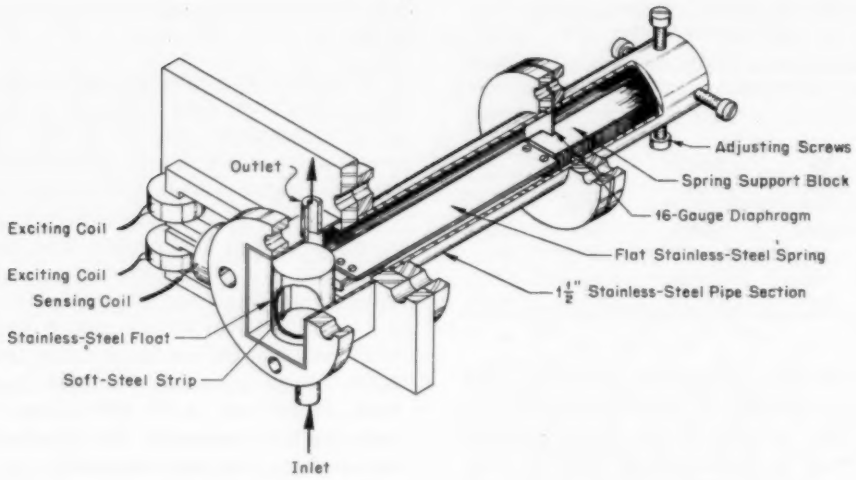

Fig. II-5 Experimental in-line densimeter.[28]

The electronic system consists of a differential transformer, a 0.33-μf condenser to resonate the transformer, a rectifier, two resistors, and a 500-μf condenser that is switched in and out to separate the column pulse and density measurements periodically. A Brown Electronik recorder completed the system.

A test reported on a simulated pulse column indicated an accuracy of ± 0.2 per cent in the range 1.000 to 1.200 g/cm^3. Tests will be made on an actual pulsed-column installation.

Argonne reports on the performance of a motor, a switch, and two types of pressure pickups in a high gamma flux.[29] Although this work was for the Experimental Breeder Reactor II (EBR-II) pyrometallurgical fuel-recycle process, the results are equally applicable to aqueous processing equipment. The equipment was subjected to gamma irradiation at levels of 1.5×10^5 to 2.1×10^6 rads/hr and a total dose of 1.0×10^9 rads. The motor (Electric Indicator Company, Inc., type ALH-541 hysteresis synchronous motor, class H insulation) lost power due to degradation of the insulation. The snap switch (Micro Switch, model 1 HT 1, High Temperature) was highly satisfactory. The (unbonded) strain-gauge pressure pickup (Consolidated Electrodynamics Corporation, type 4-316A) was satisfactory, whereas the quartz pressure pickup (Kistler Instrument Corporation, model 701) showed sensitivity to radiation which rendered it ineffective under these conditions.

Plant Design and Operation

For some time it has been felt that it would be desirable to evaluate a fuel-cycle process facility directly associated with a specific reactor. Such a concept has been studied very carefully by the Phillips technical group associated with the ICPP. This has culminated in a feasibility report[30] on a small-scale aqueous processing plant as applied to the Dresden Nuclear Power Station. Principal design considerations as stated are:

1. Limited extension of existing technology
2. Minimization of plant investment through compact plant design and maximum use of existing reactor facilities
3. Minimization of operating manpower through extensive use of automatic controls
4. Emphasis on safety and minimization of hazards

The design features are worked out and presented in detail. Both capital and operating costs are presented (1.02 mills/kw-hr was reported). Safety is evaluated with respect to both nuclear incident and chemical explosion hazards.

The plant is designed to recover 99 per cent of the uranium and plutonium from 163 Dresden fuel elements per year during 270 days of operation. Uranium and plutonium products are

shipped from the plant as completely decontaminated nitrate solutions. The main process equipment is contained in a single, relatively small, underground concrete cell designed to accommodate any reasonably credible accident. Equipment is supported from a top shielding plug, and assemblies can be decontaminated separately, remotely disconnected, and extracted as a unit for direct maintenance.

Salient design features of the conceptual plant are as follows:

1. Whole fuel elements from which the Zircaloy-2 box has been stripped are disassembled into individual fuel pins by sawing under water. The pins are fed into a dissolving vessel through a guillotine which chops the pins into smaller segments and exposes the uranium dioxide pellets. The exposed pellets are dissolved in nitric acid, and the residual Zircaloy-2 cladding segments are mechanically removed from the dissolver for disposal. Uranium and plutonium as nitrate solution are decontaminated and partitioned in a Purex solvent-extraction process.

2. Sufficient processing of liquid and gaseous plant effluents is provided to reduce the radioactivity discharged to the environs to at least the maximum permissible concentration and in most cases to well under the acceptable limits. Pending development of ultimate disposal methods, process residues are stored in suitable underground facilities located on the site.

3. With the exception of waste-disposal facilities and raw-material and product storage, the entire plant is enclosed in a 65- by 65-ft building of standard construction, located jacent to the existing fuel-handling building at Dresden. Facilities within the process building include the fuel disassembly pool, the main process cells, a cold-feed makeup area, a plutonium-product storage vault, and control room.

4. The main process equipment is contained in a single underground concrete cell 12 ft square by 35 ft deep. Functional groups of equipment are compactly mounted on a supporting grid that is hung from a top shield plug. Each unit assembly can be decontaminated separately, remotely disconnected, and extracted as a unit for direct maintenance. Four such units comprise the major process line. Mechanical equipment units requiring more frequent maintenance are mounted in extractable subassemblies. Radioactive analytical facilities are contained in a shielded cave adjacent to the process cell. Samples for analysis are continuously circulated from the process cell through sample stations in the cave. Cold and low-level samples are analyzed in a laboratory area next to the high-level analytical facility; plutonium samples are handled in a glove box. Plutonium ion-exchange and packaging facilities are contained in an airtight hood served by glove ports and air locks. A 4- by 4- by 10-ft-deep underground pit adjacent to the process cells contains intermediate waste-handling equipment.

5. Cold laboratories, maintenance shops, decontamination facilities, exhaust stack, and general services provided for the reactor are believed adequate for the processing facility.

A building perspective is shown in Fig. II-6. Some of the more outstanding features are reviewed briefly here.

The fuel elements contained in a 4.4- by 4.4- by 135-in. Zircaloy-2 casing are first cut free from casing and baffles under water on a 5-gang band saw without sawing into the uranium oxide. The entire saw tilts so that elements can be loaded vertically and clamped (these elements are very limber) and returns to the horizontal position for sawing. A chain then transfers the rod segments or pins to a fuel chopper. The fuel-pin chopper is located in the head-end top closure. Two gate valves are used as a gas lock, and the chopping is effected by a hydraulic cylinder-powered shear designed to shear pins to $3\frac{1}{2}$-in. lengths and to drop them directly into the dissolver.

The dissolver is a recirculating type, 7 in. in diameter by 11 ft long, with a removable basket for removing the undissolved Zircaloy-2 after nitric acid dissolution of the uranium dioxide pellets. Probes for a density recorder-controller and liquid-level indicator are provided. Density controls the acid addition rate. Provisions are also made for sampling, nitrogen and oxygen addition, and for airlifting the dissolver product to one of two sets of run tanks. Caustic scrubbing and condensing are provided for the dissolver off-gas. The rare gases are cold trapped and stored for future disposal.

Equipment for three cycles of solvent extraction occupies a 9- by 12-ft submerged area adjacent to the head-end equipment. The waste and product evaporators as well as acid-recovery equipment are also located here.

Table II-3 shows the important pulse-column dimensions. Active lengths of plate sections were made to conform to those in the Oak Ridge Purex pilot plant,[31] which was designed to handle a slightly higher capacity than this conceptual plant. It was felt that, by using advanced cartridge designs as developed at Hanford,[32] column heights could be materially reduced.

Three thermosyphon evaporators are provided to concentrate continuously the product from one solvent-extraction cycle for feed to the next, or for product storage. Each has a steam chest in one leg, instrument probes in the other, a steam stripper above the vapor plenum, and a condenser at the top of the steam stripper. Three thermal syphon waste evaporators, similar to the product concentrators but without steam strippers, serve a twofold purpose: (1) to concentrate the solvent-extraction wastes to as small a volume as feasible and (2) to recover decontaminated nitric acid from waste streams by distillation. The evaporators are so arranged

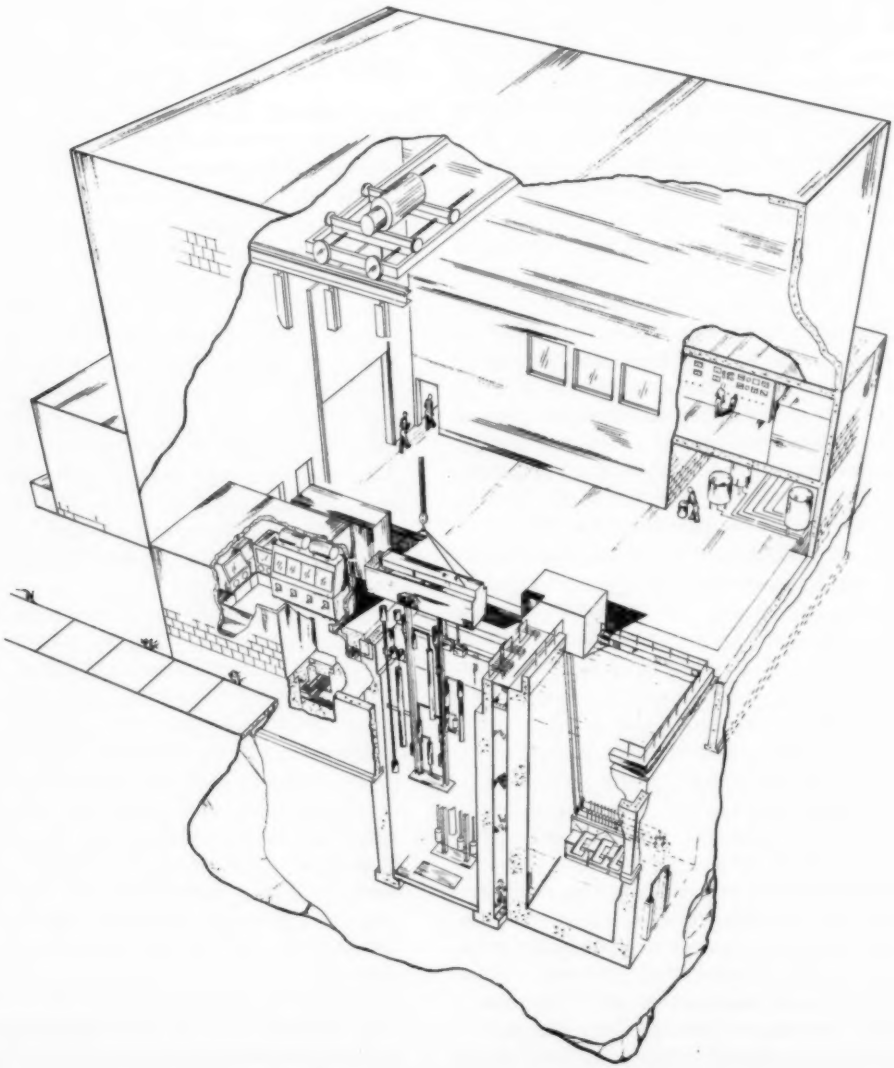

Fig. II-6 Fuel-processing building for conceptual small-scale plant.[30]

that the uncondensed vapor from the high-level waste evaporator becomes the feed to the intermediate-level waste evaporator, and its vapor in turn feeds the process-equipment waste evaporator.

Used solvent from each cycle is cleaned and recycle separately in sets of two mixer-settlers in series. Each mixer-settler has a 4- by 4-in. mixing chamber and a 4- by 8-in. settling section; both sections are 6 in. high. The impeller, slots, and baffles are arranged as described by Davidson.[33]

All solution transfers under both normal and unusual operation are made by airlift or steam jet, except where exact flow control is required for optimum operation. Where flow control of a process stream is required, the metering device is located in a separately removable probe for ease of maintenance. No valves or orifice plates are located below the top closure.

Three anion-exchange resin columns for final plutonium purification, and associated tanks and plumbing, are contained in a totally enclosed "glove-box" hood. Each column is a 30-in. length of $3\frac{1}{2}$-in. pipe packed with Dowex 1 anion-exchange resin. A stainless-steel fritted disk at either end contains the resin. Spent resin can be replaced by valving off the column and replacing with a new column.

Two hold tanks, each 20 in. in diameter by 4 ft long, are provided as one-day batch tanks for uranium product. Product solution is airlifted to these tanks from the uranium tail-end cell. Lines from each tank to the partition-cell intercycle hold tank provide means for rerunning material if product specifications are not met. After analysis, the tank content is run down by gravity to the final 7000-gal storage tank, capable of receiving 140 days' production of uranyl nitrate solution. The uranium product is shipped as slightly acid 1.5*M* uranyl nitrate solution by railroad tank car to a uranium processor for conversion to uranium trioxide. This method of shipment is safe with respect to criticality so long as the specified enrichment limits are not exceeded, i.e., no material over 1.5 per cent enrichment is handled. Freezing out of uranyl nitrate hexahydrate from the solution does not constitute a criticality hazard, since the resulting concentration would still be well below that which is critically safe for 1.5 per cent enriched material.

Table II-3 PULSE-COLUMN DIMENSIONS[30]

Column		Over-all length, ft	Active length, ft	NPS, Schedule 40	
Cycle	Function			Plate section, in.	Disengaging section, in.
HA, IA, ID	Extraction	17	12	$2\frac{1}{2}$	4
	Scrub	23	18	$2\frac{1}{2}$	4
IB	Partition	23	18	$2\frac{1}{2}$	4
	Scrub	13	8	$2\frac{1}{2}$	4
HC, IC, IE	Strip	17	12	$3\frac{1}{2}$	8

In general, the same standard industrial instruments utilized by others for solvent-extraction processes were specified for this conceptual plant. The instrument sensors for radioactive streams which are apt to require maintenance, e.g., *p*H electrodes for caustic scrubber control, are located in probes extending through the process cell shield plug or in instrument blisters atop the cell closure. Air-purge probes, instrument sensors, and electrodes were selected on the basis of minimum holdup, rugged construction, minimum size, corrosion resistance, and low response lag. Wherever possible, sensors are specified which will provide electrical output signals for an electronic indicator-recorder-controller system or a sequential indicator-monitor-alarm system. The electronic controllers are specified for a-c electrical outputs to an electropneumatic relay located at a pneumatic control valve or a chemical feed pump with pneumatic stroke length control.

Economic evaluation, resulting in the cost figure of 1.02 mills/kw-hr, is based on detailed calculations for each vessel and column. These figures were compared with actual costs of similar equipment. Installation costs of vessels were based on a percentage of cost (30 to 50

per cent, depending on complexity). Piping was based on direct labor-to-material ratios, for pipe of the same size under similar circumstances. The in-cell ratios covered the range from 6 to 1 to 1.2 to 1. The out-of-cell range was from 3.2 to 1 to 1 to 1. Total investment costs were calculated to be $4 million, and operating costs were estimated to be $617,000 per year (51 total workers plus materials).

Du Pont has issued a report[34] describing studies on power-reactor fuel processing which covers conceptual designs for six specific combinations of plant capacity up to 10 tons of uranium per day and which gives estimates of capital and operating costs. Costs are discussed in Sec. I under "Fuel-Processing Costs." The report includes design data, process and engineering description, alternate plant designs and flow sheets, service diagrams, and miscellaneous drawings. The concept possesses a number of interesting design features.

Equipment in the high-level canyon would be maintained with a remotely controlled crane. Viewing would be done with television cameras mounted on the crane. General lighting as well as television lights on the crane would be used.

For canyon vessel connections, a typical jumper design employing spherical seats would be used. Only a reasonable number of spare wall nozzles would be required. Floor flushing and fire spray would be included under the canyon blocks. Thermocouples would be used for fire detection.

All canyon pumps would be of the overhung shaft design similar to Fig. II-7. Bearings are to be made of carbon steel and are to be the prepacked and sealed-for-life type. No lubrication jumpers are required for this type bearing. Pump motors are to be special design high-slip, three-phase, explosionproof, induction type using AIEE type F insulation. This conceptual motor design would permit operation for extended periods at reduced voltage and speeds so that pumping rates could be varied using variable voltage transformers where accurate rate control is not required. Where accurate rate control is required in the canyon, such as on the mixer-settler feeds, a control valve with a bellows seal on the stem and a transmitting type rotameter would be used. All canyon pumps are to be provided with a bypass on the normal discharge line which would return liquid back to a mixing jet within the tank on which the pump

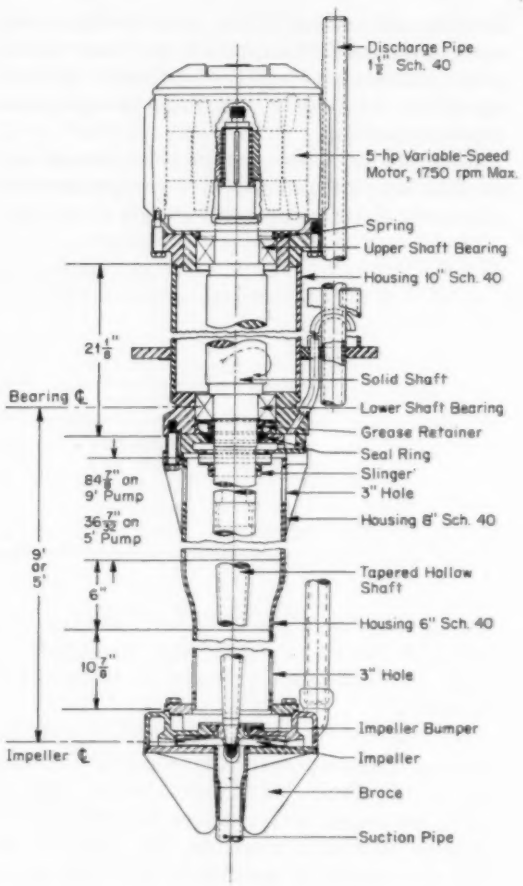

Fig. II-7 Pump design for radiochemical process plant.[34]

is located. This would eliminate the need for separate agitators on the canyon vessels.

The proposed dissolvers are of the batch type with a downdraft condenser for acid return. Coating removal and acid dissolution are separate steps. Off-gas would be filtered through glass fibers (Fig. II-8). A vertical basket type centrifuge would be provided for silica removal using gelatin as a coagulation aid.

Solvent extraction would be carried out by use of 12- or 18-stage mixer-settlers (Fig. II-9). Each stage has a volume of 75 gal. All mixing motors on each unit are to be on a single electrical circuit, and each is to have its own variable-frequency generator (150 to 600 rpm). Feed rates are controlled by a rotameter control valve located in the feed jumper.

The dilute uranium stream from extraction would be concentrated in a conventional natural-circulation evaporator. Two dry bubble-cap trays would be used for deentrainment. Since some alpha activity can be expected to pass overhead, this stream would be sent to the general-purpose evaporator before disposal to the ground. The concentrated uranium would be passed through silica-gel columns to effect final cleanup of any particulate matter and to remove traces of niobium-zirconium activity.

A Higgins continuous ion bed would be used for anion exchange to concentrate the plutonium to ~40 g/liter and at the same time provide some additional decontamination. For the final concentration of 250 g/liter, a continuous natural-circulation evaporator would be used.

For solvent treatment, simple mixer-tank arrangements are used for washing. The proposed system also incorporates a vacuum still that has capacity to fractionate any one of the three solvent systems in 48 hr.

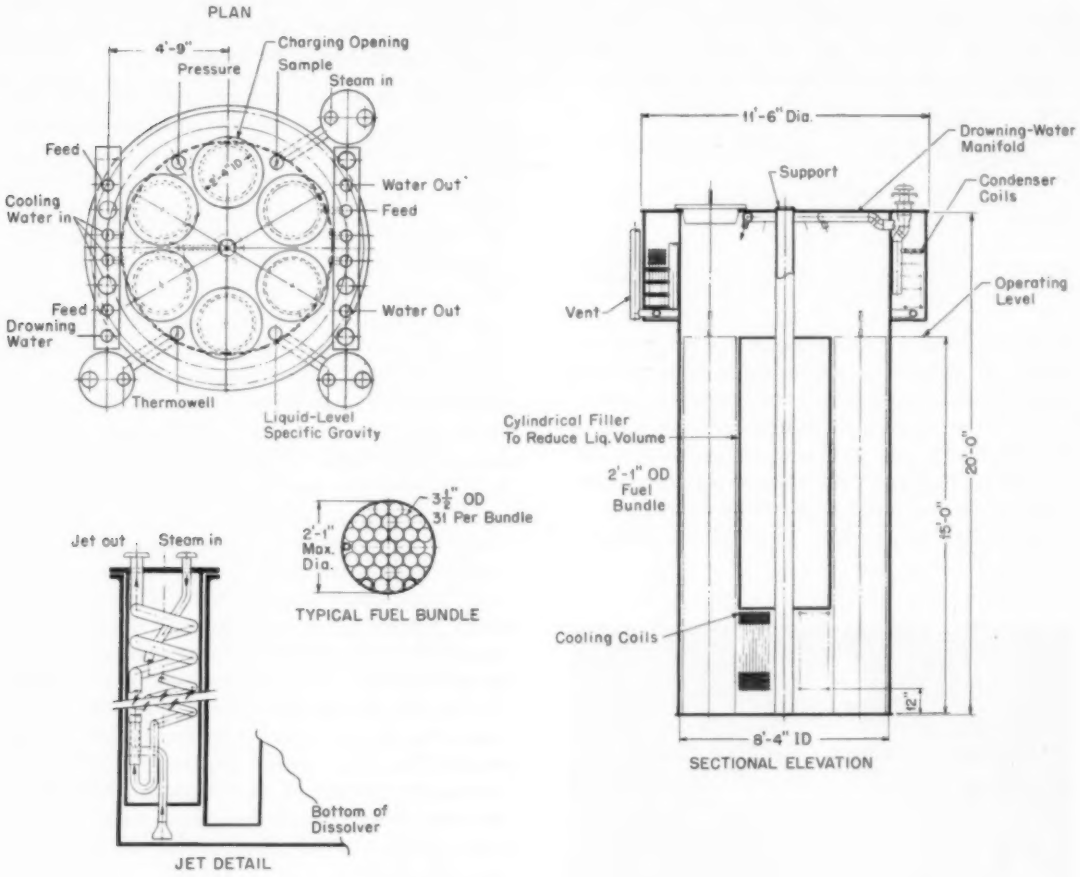

Fig. II-8 Proposed design of natural-uranium dissolver.[34]

High-activity waste is concentrated, neutralized, and stored. The evaporator is a natural-circulation, continuous draw-off type, with bubble-cap deentrainer. Steam pressure is limited to 25 psig to avoid initiating explosive reactions between any organic material and nitric acid. Low-activity waste would be treated in a similar manner to the high-activity material, and reevaporation of the overhead from the high-activity waste evaporator would be accomplished in the low-activity system. There is also included a batch evaporator for miscella-

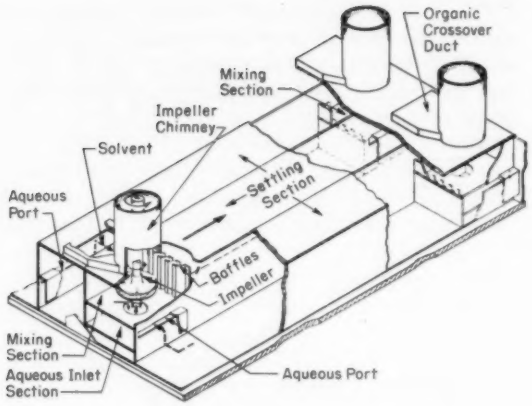

Fig. II-9 Isometric view of mixer-settler stages.[34]

neous materials such as spills and flushing solution. A general-purpose evaporator is also proposed for further decontamination of overheads from various evaporations, as well as laundry wastes, purge from storage basins, etc. This is a two-stage unit, and overhead from the second stage is sent to the stack as a vapor. A stack heater is provided to prevent condensation.

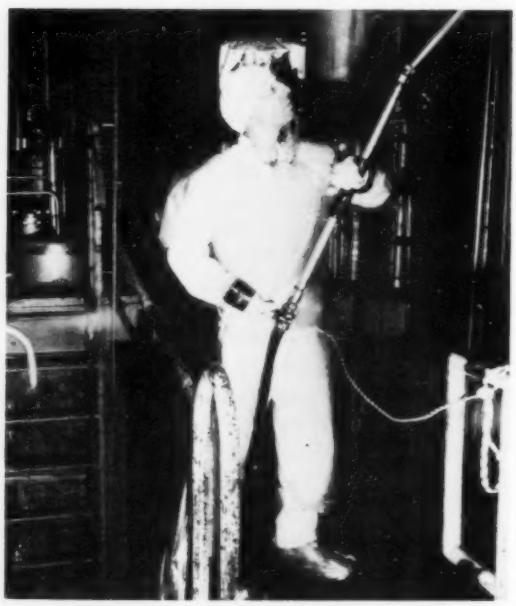

Fig. II-10 Cell 6 decontamination with Sellers steam jet.[35]

The storage tanks provided for waste are of concrete lined with carbon steel. Cement grout is placed directly under the steel with grooves for leak detection. Condensers and airlift circulators are provided to take care of the heat generated. The low-level waste would be further evaporated at the tank farm until the solids content is 70 per cent, so that on cooling a crystalline mass will be formed.

Further detail is given on proposed cold feed preparation, fume recovery and acid concentration, laboratories and sampling, service facilities, ventilation, basin water treatment, rolling stock and machinery, and emergency power. The appendix contains many supporting data, especially on cost analysis.

ORNL reports[1,35] on the cleanup of cells 6 and 7 of their pilot plant following the plutonium evaporator explosion[36] late in 1959. It was reported that 521,000 liters of various decontaminants have been used to reduce alpha contamination by a factor of 1000. After the plutonium was removed from the interior of the equipment, the decontamination of the cells was started. A reverse transparent glove box "greenhouse" was used at the entrance of the cell, from which a man could spray down the walls and observe or direct operations. Then the block walls and debris were removed using 55-gal drums with plastic-bag containment. Finally it was possible for a man with an air suit (Fig. II-10) to enter and spray the walls, equipment, etc., with a steam jet. Table II-4 shows the amounts of plutonium recovered from various equipment items. Anion exchange was used to recover the plutonium from an evapo-

Table II-4 PLUTONIUM REMOVAL FROM CELL EQUIPMENT[35]

Equipment components	Flushes		Plutonium removed	
	No. used	Volume, liters	Grams	% of total
Feed preparation	1	1,510	2.03	0.1
Solvent extraction	17	12,250	45.77	3.0
Evaporators:				
P-65	7	3,865	21.54	1.4
P-15*				
Body	40	15,879	804.26	51.9
Catch tank	7	2,105	492.58	31.7
Exterior	91	252,610	184.90	11.9
Total	163	288,219	1,551.08	100.0

*Ruptured evaporator.

rated solution. Numerous charts and curves recording the progress of the cleanup are presented.

Construction Materials

A modification of the Zirflex process by ORNL for the processing of high-uranium-content zirconium fuels has been previously reported.[37] The modification consists of the addition of hydrogen peroxide to the Zirflex dissolvent. Corrosion tests presented at that time indicated that the peroxide addition reduced the corrosion rates of several alloys. The rates of attack were sufficiently low to provide an incentive for conducting more extensive continuous-flow experiments. The tests were conducted in the dissolver solution (5.4*M* ammonium fluoride–0.33*M* ammonium nitrate–0.003*M* hydrogen peroxide) presently proposed for use with the high-uranium zirconium fuels.[38–40] The flow rate through the test vessel was such that a complete change of solution occurred every 45 min. Samples were taken frequently to ensure the maintenance of the peroxide level. The alloys tested were stainless-steel types 304L and 309SCb, Hastelloy F, and LCNA (low-carbon Nionel). The results of the test are shown in Table II-5. The significant attack on all alloys occurred at the interface or in the solution; attack in the vapor phase was not severe. The surface corrosion rates of stainless-steel type 309SCb, Hastelloy F, and LCNA were all in the range of 1 to 3 mils/month. Localized and subsurface attacks were observed in all three alloys; however, this attack was considered minor in the case of stainless-steel type 309SCb and LCNA. With respect to the change of corrosion rate with time, the behavior of LCNA was better than that of stainless-steel type 309SCb in that the final observed corrosion rate for LCNA was approximately one-half the rate observed after 24 hr of exposure. In the case of type 309SCb stainless steel, there appears to be a slight increase of corrosion rate with time. It was concluded that LCNA appears to be a satisfactory construction material for a modified Zirflex dissolver.[40] To complete the study of construction materials for this process, it is now planned to conduct similar tests with partially spent dissolver solution.

Table II-5 CORROSION OF VARIOUS WELDED ALLOYS IN MODIFIED BOILING ZIRFLEX DISSOLVENTS[1,38–40]

(Composition: 5.4*M* NH_4F; 0.33*M* NH_4NO_3; 0.003*M* H_2O_2)

Alloy	Exposure time, hr	Corrosion rate, mils/month			Comments relating to interface and solution exposure
		Vapor	Interface	Solution	
S.S. 304L	24	0.85	14.8	16.1	Extensive end corrosion and pitting
	476	0.23	11.6	12.9	
S.S. 309SCb	24	0.30	1.3	1.6	Random pitting; some localized pitting at weld-base metal junction
	500	0.07	2.2	2.2	
Hastelloy F	24	0.5	2.9	2.7	Severe weld decay and pitting
	504	0.4	2.9	2.9	
LCNA*	24	0.1	2.4	2.3	Some grain-boundary attack in heat-affected zone
	504	0.5	1.1	1.1	

*Low-carbon Nionel.

One of the fuels for which the above process is intended is the TRIGA core alloy. Prior to dissolution of this material, it is necessary to decompose the graphite plugs in the fuel assembly. A mixture of 90 per cent fuming nitric acid–10 per cent fuming sulfuric acid at relatively low temperatures has been proposed for the decomposition. Type 309SCb stainless steel and LCNA were exposed to this environment[40] at 50°C for 336 hr. Maximum rates of attack observed were 2.9 and 0.90 mils/month, respectively. In both cases the maximum rates were observed on specimens exposed in the vapor phase. This was due mostly to extensive subsurface attack in the form of weld decay and intergranular penetrations. Neither alloy is considered suitable for this type of service. It

is reported that INOR-8 was also tested in the dissolvent proposed for the TRIGA fuel at 50°C. The corrosion observed over a 336-hr exposure was 0.17 mil/month in both the solution and vapor phases. No localized attack was observed.

Both Hanford and ORNL have contemplated a common processing facility for the handling of stainless-steel fuels by the Sulfex process and zirconium-matrix fuels by the Zirflex process. Hanford is also considering the possibility of utilizing the same equipment for Niflex processing of stainless-steel fuels. A report evaluating the use of Nionel and Hastelloy F for such purposes has been published by ORNL.[41] The analysis presented reaffirms ORNL's belief that Nionel is the logical choice and gives the reasons for the rejection of Hastelloy F. The report suggests that, if Niflex processing needed to be considered for the Oak Ridge process, Hastelloy F might be considered.

Although ORNL has appeared to be satisfied with Nionel for the combination of Sulfex and Zirflex processing methods, testing of other experimental alloys has been continued. The most recent of these include Haynes experimental alloys designated EB4358 and EB5459. In the initial Sulfex dissolvent (6*M* sulfuric acid), these alloys show a small but insignificant decrease in corrosion rate relative to Nionel. The improvement is more marked in solutions containing 10 g of stainless steel per liter (0.47 and 0.52 mil/month, respectively, as compared to 1.7 mils/month for Nionel). Whereas Nionel showed a maximum corrosion rate in the vapor phase, both of the experimental Haynes alloys were corroded less rapidly in the vapor phase than in the solution phase. All three materials have shown some random pitting in the solution.[1]

Titanium has been selected by both ORNL and Hanford as the construction material for the Darex processing of stainless-steel-matrix fuels. It was reported in an earlier Review[18] that Oak Ridge was making efforts to extend the use of titanium to the processing of zirconium fuels in fluoride systems. More recently, the possibility of extending the use of titanium dissolution equipment to the handling of uranium-molybdenum fuels has been examined.[1] The best dissolvent for this fuel is considered to be nitric acid–ferric nitrate. Welded specimens of titanium-45A were exposed to 3.5*M* and 8*M* nitric acid–0.5*M* ferric nitrate–0.6*M* uranyl nitrate–0.02*M* molybdenum trioxide. Erratic behavior of the titanium in the first one to three days of exposure was observed. At longer exposure times, rates were no longer erratic and slowly decreased. After 1000 hr the maximum rates of attack observed were 0.06 mil/month, and no subsurface or localized attack was evident.

A topical report on the aqueous processing of uranium-molybdenum alloys has been published by ORNL.[6] This report includes corrosion information which has been previously presented in past issues of *Reactor Fuel Processing*.

In an earlier issue of *Reactor Fuel Processing*,[2] information was presented from Savannah River on the corrosion characteristics of stainless-steel type 309SCb (existing dissolution equipment at Savannah River is made of this material) in mixtures of nitric and hydrofluoric acids. This was directed toward the possible processing of zirconium-clad fuels in this equipment. Brookhaven National Laboratory is continuing studies in this processing system (presumably for Savannah River), not only for possible application of this system to zirconium-matrix fuels, but also to stainless-steel fuels. Savannah's information indicated that the corrosion rate of stainless-steel type 309SCb was a minimum at a nitric acid concentration of 1*M* for several hydrofluoric acid concentrations. As a result, the current work at Brookhaven is being conducted with 1*M* nitric acid–0.1*M* hydrofluoric acid. This environment is similar, but not identical, to the Niflex dissolvent proposed and used by Hanford. Brookhaven has obtained corrosion rates in this system in the range of 35 to 40 mils/year,[42] a factor of 2 to 3 greater than the rates obtained at Savannah River. Excessively high corrosion rates were found in the vapor phase. However, it was learned that this can be reduced to acceptable levels by sparging the solutions with air.

The ICPP has been investigating processing methods for fuel from the Heat Transfer Reactor Experiment (HTRE). The fuel elements consist of thin ribbons of a uranium dioxide–Nichrome matrix which are clad in a niobium-modified Nichrome cladding.[43] Laboratory studies have indicated that maximum dissolution rates are obtainable with a mixture of 4*M* hydrochloric acid and 6*M* nitric acid. Corrosion investigations for this process centered about

titanium. Samples, in both the stressed and welded form, were exposed to various acid mixtures. In some experiments a negative potential of 1.5 volts was applied so that hydrogen ions would tend to migrate to the titanium and enhance the possibility of hydrogen embrittlement. In addition, duplicate experiments were performed with the titanium in contact with dissolving Nichrome V. A ternary diagram showing the various areas of acceptable and unacceptable corrosion rates is shown in Fig. II-11. In

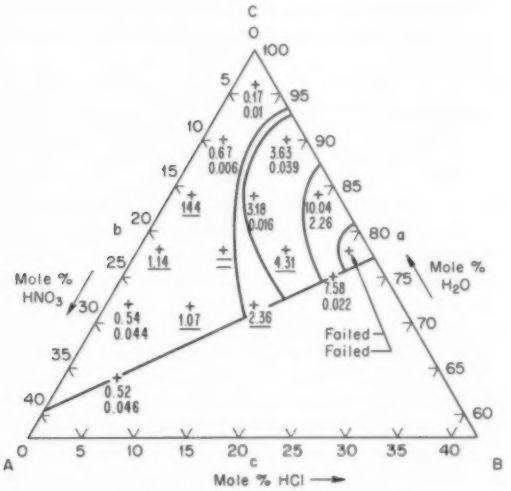

Fig. II-11 Corrosion of 75A titanium in the system[43] HCl-HNO_3-H_2O.

general, corrosion resistance was poor when the mole fraction of hydrochloric acid exceeded that of nitric acid. With dissolving Nichrome V present, rates of attack were less than 0.05 mil/month in those solutions in which the attack was less than 1.4 mils/month in the uncoupled form. No evidence of hydrogen embrittlement or stress corrosion was found.

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility processes based on both fluoride and chloride systems, pyrometallurgical and other high-temperature processes, and certain electrolytic processes are among nonaqueous processes under development for separating valuable materials from used reactor fuels. Although some of these methods are being considered as head-end operations for solvent-extraction processes, most of the methods are complete processes of either the high- or low-decontamination type. The latter type, such as the pyrometallurgical processes, is designed to be used in conjunction with remote fuel refabrication techniques. None of the nonaqueous methods are yet in use in processing plants, but the construction of a pyrometallurgical process facility for the second Experimental Breeder Reactor (EBR-II) is nearly completed.

Volatility Processes

The volatilities of uranium and plutonium hexafluorides have been proposed as a basis for processing various types of irradiated nuclear reactor fuels. Liquid-phase fused-salt processes are being considered for application to the recovery of uranium from molten-salt reactor fuel and from zirconium-uranium alloy fuel. Solid phase–gas phase halogenation processes have also been proposed for application to zirconium-uranium alloy fuel and to uranium dioxide fuels. Fluidization techniques are employed in some of these dry halogenation processes to enhance process control. This review summarizes (1) the results of laboratory-scale dissolution of reactor fuels in liquid nitrogen dioxide–hydrogen fluoride, (2) the recent developments in fused-salt processing of uranium-zirconium alloy fuel elements, and (3) the physical and chemical properties of fluoride compounds of process interest.

Liquid-Phase Halogenation Processes

Laboratory-scale work has continued at BNL on the nonaqueous nitrogen dioxide–hydrogen fluoride system for processing reactor fuel elements.[1] Monel equipment capable of dissolving up to 100 g of alloy fuel has been constructed and tested. The equipment consists of a dissolver, evaporator, condenser, traps for volatile materials, and associated equipment for measuring the volumes of nitrogen dioxide and hydrogen fluoride added to the system.

Data on the vapor pressure–composition–temperature relations of the nitrogen dioxide–hydrogen fluoride system have been reported.[1] The composition range 2.4 to 30 mole % nitrogen dioxide in hydrogen fluoride was studied over the temperature range 30 to 100°C.

Sintered thorium dioxide–uranium dioxide fuel material does not react with the Nitrofluor solvent. A survey of various nonaqueous solvents produced a good solvent for the ceramic fuel,[1] monofluophosphoric acid (H_2PO_3F). Pellets of ceramic fuel readily dissolved in the acid at 100°C. The reaction product was very soluble in the liquid, even at room temperature. It was possible to recover both uranium and thorium in good yield as hydrous oxides by adding the solution to water and neutralizing the acid with sodium hydroxide. A Thorex solvent-extraction feed solution may be prepared by dissolving the hydrous oxides in 1.6*N* nitric acid. Alternatively, uranium might be recovered as uranium hexafluoride by treating the dried oxides with bromine trifluoride. A single trial demonstrated 99.8 per cent recovery of uranium hexafluoride by this method.

Initial experiments on corrosion of materials in monofluophosphoric acid indicate that copper is the only common construction material with good resistance to the acid. However, under certain conditions during dissolution of the

ceramic fuel, the observed penetration rate of copper specimens was as high as 22 mils/month.

Addison and Hodge[2] have reported experimental work on the dissolution of uranium metal and halides in a nonaqueous system of dinitrogen tetroxide–nitrosyl chloride (N_2O_4-NOCl). Uranium metal does not react with dinitrogen tetroxide alone but does react with liquid nitrosyl chloride and with mixtures of the two solvents. The concentration of nitrosyl chloride in dinitrogen tetroxide must be above 40 wt.% before perceptible reaction occurs. The reaction mechanism involves initial attack on the uranium metal by nitrosyl chloride to form solvated uranium tetrachloride, followed by oxidation and solvolysis of the chloride by dinitrogen tetroxide. The product is the addition compound $UO_2(NO_3)_2N_2O_4$. A striking feature of the reaction between metallic uranium and the dual solvent is that the nitrosyl chloride concentration can be increased to 84 wt.% before any chloride appears in the product. Uranyl compounds are always formed in the presence of dinitrogen tetroxide; with mixtures containing only 2 per cent dinitrogen tetroxide, no uranium tetrachloride appears in the product. Solvated uranium tetrachloride is the only product of the reaction between uranium metal and pure nitrosyl chloride.

Fused-Salt Processes

Application to Zirconium-Containing Fuels. An ORNL report[3] summarizes recent developments in the Volatility Pilot Plant for processing uranium-zirconium alloy fuel elements.

The basic fluoride-volatility flow sheet (Fig. III-1) involves dissolution of fuel elements in molten NaF-LiF-ZrF_4 (37.5 to 37.5 to 25.0 mole %) by hydrogen fluoride, fluorination of uranium tetrafluoride to hexafluoride with fluorine, further purification by adsorption on and desorption from a sodium fluoride bed, and recovery of uranium hexafluoride in a cold trap. Processing conditions tentatively fixed as a result of recent experimental runs are: (1) dissolution temperature 50°C above the salt melting point (in most cases the temperature was initially 650°C and gradually decreased to 500°C as dissolution proceeded), (2) hydrogen fluoride flow rate of 150 g/min, (3) the use of movable-bed adsorbers rather than the fixed-bed adsorbers, which were used previously and will be available for emergency use, and (4) the use of a small product receiver to recover for sampling the uranium hexafluoride from each individual run followed by transfer of product from several runs to the larger shipping cylinder. The fluorine flow-rate variable is still being studied.

The first seven development runs (T-1 to T-7, Table III-1) were runs in which simulated Zircaloy-2 fuel elements were dissolved to determine the operability of the dissolution system. A major operating difficulty was encountered in the form of plugging of the dissolver off-gas valves by 0.01- to 2-μ particles formed in the dissolver during dissolution. The particles appeared to be 25 to 40 per cent salt, the remainder being metal, principally iron, tin, chromium, nickel, and molybdenum. The average concentration in the off-gas during a dissolution was about 1 g/m^3. Filtration with copper mesh, which provided a large amount of impingement surface, was the most successful method tried for removing the particles; it was 85 to 92 per cent efficient as the dust loading on the filter increased from 0 to 18.0 lb/cu ft. Filtration by porous metal and separation by a 2.5-in.-ID cyclone were even less satisfactory. A system for continuous washing of the off-gas line with liquid hydrogen fluoride is being designed.

The first seven of a series of complete flow-sheet demonstration runs (TU-1 to TU-7) with nonirradiated fully enriched zirconium-uranium alloy fuel elements were completed. A total of 3579 g of uranium was processed. Approximately 531 g of uranium was retained in recoverable-form samples, residue on sodium fluoride adsorbers, and cylinder heels. The system holdup was determined to be 200 ± 100 g. Fuel dissolution rates were >3.5 kg/hr with a hydrogen fluoride flow rate of 150 g/min (Table III-1). In fluorination of the uranium tetrafluoride to hexafluoride with fluorine flow rates from 4 to 16 standard liters/min for 85 to 150 min, the uranium loss to the waste salt was less than 10 ppm (Table III-2). There were no serious difficulties in the adsorption of uranium hexafluoride on and desorption from sodium fluoride. Nonrecoverable uranium losses averaged less than 0.8 g per run or about 0.1 wt.% of the fuel charged.

Cation impurities in the uranium hexafluoride product varied widely (Table III-3), and no explanations of these variations are available

at present. In the case of sodium, the use of the movable-bed adsorber in Run TU-2 and subsequent runs would have been expected to result in sodium contents less than 600 ppm but greater than 10. Holdup of sodium fluoride in the lines is a possible factor in this result.

Engineering-scale studies on sorption of uranium hexafluoride from a flowing uranium hexafluoride–nitrogen stream by a deep fixed bed of granular sodium fluoride indicated that the removal rate is controlled by the diffusion of uranium hexafluoride through the solid phase and through the film and by the rate of heat transfer between the solid and the gas stream. The importance of each process depended on flow rate, gas concentration, and initial solid temperature. Calculated film coefficients for mass transfer of uranium hexafluoride are about 0.05 cm/sec and for solid-phase diffusivities, about 10^{-5} cm^2/sec.

A monitoring system for continuously determining the uranium hexafluoride concentration in the range 100 ppm to 20 mole % in a uranium hexafluoride–nitrogen mixture, which uses a Thermistor cell to sense effects due to the change in density of sample gas with change in uranium hexafluoride concentration, showed a response time of less than 10 sec.

One of the fission-product fluorides that is volatilized at fluorinator temperatures is molybdenum hexafluoride; the reactions of molybdenum hexafluoride with the sodium fluoride adsorber were studied to determine its effectiveness in removing molybdenum hexafluoride from the uranium hexafluoride stream. Laboratory-scale measurements of the dissociation pressure of the molybdenum hexafluoride–sodium fluoride complex indicated that molybdenum contamination in the product uranium hexafluoride can be minimized by proper choice of adsorption temperature and fluorine flow rate. As with the uranium hexafluoride–3 sodium fluoride complex, the classical relation between dissociation pressure and temperature exists over a wide range in the ratio of sodium fluoride to molybdenum hexafluoride. The data in Fig. III-2 were based on ratios of sodium fluoride to molybdenum hexafluoride of 5.4 to 248. The molybdenum hexafluoride–sodium fluoride complex is colorless in contrast to the yellow uranium hexafluoride–sodium fluoride complex; they are alike in being stable to

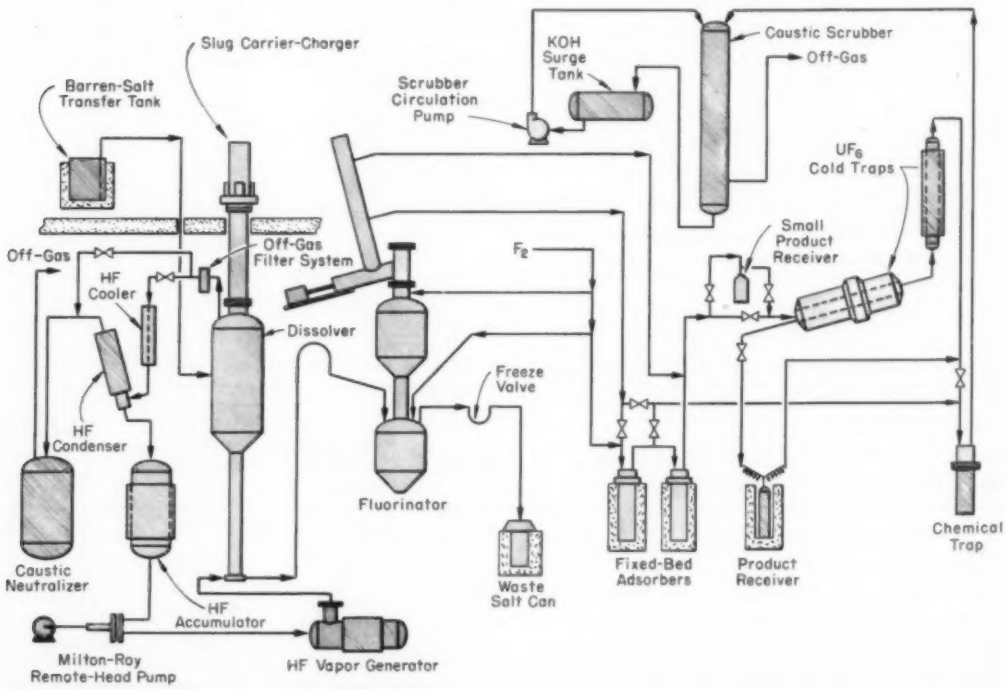

Fig. III-1 Schematic diagram of the ORNL Volatility Pilot Plant.[3]

oxygen and nitrogen but not to water, which causes hydrolysis of the molybdenum complex.

Corrosion rates in the INOR-8 dissolver were obtained during the 14 nonradioactive dissolution runs (Table III-1). With total salt and hydrogen fluoride exposure times of 765 and 404 hr, respectively, the maximum decrease in metal thickness based on ultrasonic measurements was 25 mils, for a rate loss of 0.06 mil per hour of hydrogen fluoride exposure or 24 mils per month of salt–hydrogen fluoride residence time. Ultrasonic measurements showed only bulk metal losses as opposed to intergranular corrosion or small pits. However, complete gamma radiography and some replication with dental wax indicated no significant pitting.

Fluorinator corrosion rates were higher than those experienced in the dissolver. Fluorine exposure during preliminary tests and the seven runs with nonirradiated uranium in the melt (Table III-2) was 20.3 hr with 694-hr exposure to salt. Ultrasonic thickness measurements indicated a corrosion rate of about 1 mil/hr based on exposure to salt-fluorine conditions. However, a life of approximately 115 runs is

Table III-1 SUMMARY OF DISSOLUTION RUNS[3]

(Runs T-1 Through T-7: Dummy Zircaloy-2 Fuel, ~30 Kg per Element; Runs TU-1 Through TU-7: Nonirradiated Fully Enriched Zirconium-Uranium Alloy Fuel, ~1 Per Cent U, ~40 Kg of Fuel per Run; Molten Salt: 37.5-37.5-25.0 Mole % NaF-LiF-ZrF_4)

Run No.	Salt temp., °C Max.	Salt temp., °C Min.	Av. dissolution rate,* kg/hr	Time,* hr	Av. HF flow rate, g/min	Av. HF utilization,* %	Salt recovery, %
T-1	560	520	0.84	32.1	104	13.5	105.5
T-2	530	525	0.69	34.6	40	28.9	97.0
T-3	625	550	1.46	20.2	90	27.0	102.6
T-4	630	495	1.45	18.5	90	26.9	101.8
T-5	625	530	1.21	22.5	90	22.4	100.1
T-6	650	500	1.20	22.0	150	13.4	99.0
T-7†	655	523	2.77	19.0	135	34.4	100.0
TU-1†	670	490	2.46	18.2	92	44.5	100.5
TU-2†	650	500	2.82	15.5	125	37.3	102.4
TU-3†	655	495	3.22	12.3	150	35.8	98.0
TU-4†	650	555	3.34	7.6	150	33.4	100.1
TU-5	650	500	2.50	15.7	150	24.5	98.1
TU-6	650	500	1.89	18.8	121	22.8	92.8
TU-7	650	500	3.68	10.8	150	35.7	106.7

* Based on 90 per cent completion of dissolution.
† Two-element dissolutions.

Table III-2 SUMMARY OF FLUORINATION DATA[3]

[Feed Salt: NaF-LiF-ZrF_4 (~27.5-27.5-45.0 Mole %); Fluorination Temperature: 497 to 515°C]

Run No.	Salt U conc., ppm Initial	Salt U conc., ppm Final	F_2 flow, liters/min at STP	Fluorination time, min	F_2 utilization,* %	Mole ratio of F_2 used* to original U	Fluorination time to obtain 10 ppm U in salt, min	Total nonrecoverable U losses Grams	Total nonrecoverable U losses Wt.%
TU-1	2830	1.2	12	150	4.9	20.6	77	0.372	0.07
TU-2	2040	3.8	6	150	11.7	8.5	55	1.227	0.28
TU-3	3003	9.1	9	105	8.9	11.2	75	1.935	0.31
TU-4	5118	5.6	4, 12†	75, 60†	8.9	11.2	97	1.006	0.16
TU-5	2205	1.0	4, 16	60, 30	6.1	16.4	63	0.236	0.05
TU-6	2667	0.7	6, 16	60, 25	5.8	17.3	56	0.177	0.04
TU-7	2201	4.2	6, 16	60, 40	4.1	24.2	86	0.277	0.06

* For minimum of 99.7 per cent conversion of UF_4 to UF_6.
† Four standard liters/min for 75 min, 12 standard liters/min for 60 min.

predicted for both vessels since the fluorination runs require only about 1.5 hr of fluorine exposure as compared to about 18 hr of hydrogen fluoride exposure per run in the dissolver.

Application to Stainless-Steel-Containing Fuels. Dissolution of stainless-steel-clad fuels with hydrogen fluoride in fused fluoride salts followed by volatilization of uranium hexafluoride is considered feasible as a means of processing stainless-steel-clad fuels. A process flow sheet based on laboratory data has been suggested for use in the Volatility Pilot Plant with the EBR-I core 2 meltdown fuel, 88 per cent uranium–2 per cent zirconium–10 per cent type 347 stainless steel plus iron container material. This flow sheet uses the high dissolution rate in 37-52-11 mole % LiF-NaF-ZrF_4 with subsequent addition of zirconium tetrafluoride to bring the composition to 26-37-34-3 mole % LiF-NaF-ZrF_4-UF_4, a composition favorable for fluorination at 500°C and with an adequate solubility for the stainless-steel fluorides. Small-scale tests of this flow sheet were successful and showed good uranium recovery. The corrosion rate for INOR-8 (the construction material currently favored for the dissolution vessel) ranged from 0.064 mil/hr for the initial composition to 0.005 mil/hr for the latter.

Table III-3 CATION IMPURITIES IN URANIUM HEXAFLUORIDE PRODUCT OF VOLATILITY PROCESS[3]

Run No.	Amount, parts per 10^6 parts UF_6									
	Cr	Cu	Fe	Li	Mo	Na	Ni	Sn	Zr	Total
TU-1	<1	10	2	<2	100	1300	3	2	<1	<1421
TU-2	<1	17	<1	<2	69	600	<1	1	<1	<693
TU-3	<1	74	5	<2	17	600	24	4	<1	<728
TU-4	1	210	6	<1	21	<10	4	4	<1	<253
TU-5	<1	4	<1	<1	61	<10	4	<1	<1	<84
TU-6,7	<1	8	2	<1	220	<10	6	2	<1	<251

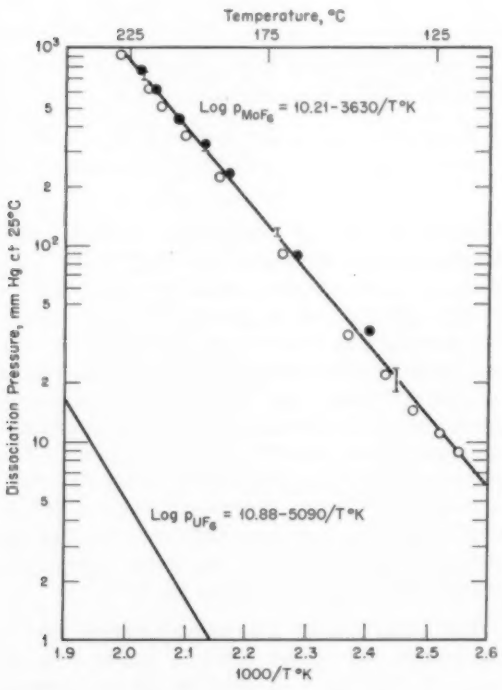

Fig. III-2 Dependence of molybdenum hexafluoride–sodium fluoride dissociation pressure on temperature: comparison with dissociation pressure of uranium hexafluoride–3 sodium fluoride complex.[3]

The dissolution rate of type 347 stainless-steel coupons was about 0.5 mg/(cm^2)(min) at 650°C in 60 to 40 mole % sodium fluoride–zirconium tetrafluoride, in which the solubilities of nickel fluoride and ferrous fluoride are high. In 26-37-37 mole % LiF-NaF-ZrF_4, a salt from which uranium can be removed by fluorination at 500°C, the rate of dissolution was 0.24 mg/(cm^2)(min). This composition of salt is believed to be the best of all compositions tested (Table III-4) for this process use.

Data for dissolution of various oxides, such as those contained in stainless-steel-clad oxide fuels, in fused salt (Table III-5) together with previously published metallic dissolution results indicate that the fused-salt volatility process may be applicable to a variety of heterogeneous fuel types. Corrosion studies of fused salt–hydrogen fluoride–oxide–water va-

Table III-4 DISSOLUTION RATES OF TYPE 347 STAINLESS STEEL IN FUSED FLUORIDES BY HYDROFLUORINATION[3]

Salt composition, mole %	Temp., °C	Dissolution rate, mg/(cm²)(min)
60 NaF–40 ZrF_4	600	0.38
	650	0.55
	700	1.1
37 LiF–52 NaF–11 ZrF_4	650	1.7–2.1
26 LiF–37 NaF–37 ZrF_4	500	0.24
	600	0.67
50 KF–50 ZrF_4	650	2.0–2.2
60 KF–40 ZrF_4	650	0.89–1.0
46 LiF–11.5 NaF–42 KF	550	9.7
	600	8.5
	650	5.5

removal was approximately proportional to the fluorine flow rate.

These data indicate that the ratio of plutonium hexafluoride to fluorine in the effluent gas is a factor of about 10^5 lower than the ratio of plutonium hexafluoride to fluorine in the equilibrium relation, $K_{equil.} = p_{PuF_6}/p_{F_2}$ for the reaction $PuF_6 \rightleftharpoons PuF_4 + F_2$.

Fused-Salt Containment by Frozen-Wall Techniques. A summary report has been issued[4] on a study of process-vessel design for frozen-wall containment of fused salt. The feasibility of containment of a molten sodium fluoride–zirconium fluoride salt at 550°C was demonstrated in test equipment of pilot-plant size. In general, heat flux at the frozen wall

Table III-5 DISSOLUTION OF OXIDES BY HYDROFLUORINATION IN FUSED SALT[3]

Material*	Salt, mole %	Temp., °C	Dissolution rate, mg/(cm²)(min)
ZrO_2	31 LiF–24 NaF–45 ZrF_4	650	1.1, 1.4
36% UO_2–64% ZrO_2	31 LiF–24 NaF–45 ZrF_4	650	1.0, 1.2
UO_2	31 LiF–24 NaF–45 ZrF_4	650	11.5
BeO	49 NaF–40 LiF–11 BeF_2	600	0.60, 0.56, 0.62
ThO_2	(Apparently much faster in 31 LiF–24 NaF–45 ZrF_4 than in any of above due to metathesis with ZrF_4; specific rates difficult to determine)		

* All high-fired materials.

por systems have been initiated, and preliminary results appear favorable for this process application.

Application to Plutonium-Containing Fuels. Initial work has been conducted to explore the effect of temperature, salt composition, and fluorine flow rate on plutonium volatilization. These tests were made at a low level of 2 ppm plutonium. The results (Fig. III-3) indicate that plutonium hexafluoride volatilization is a first-order reaction under the conditions used. Although the reaction is bimolecular, it seems probable that the activity of fluorine in the tests was fairly constant, thus making the rate of plutonium hexafluoride volatilization proportional only to the plutonium concentration in the salt. The first-order effect, however, might be partly due to the rate of removal of gas from the free space above the fused salt. The effect of salt composition and temperature was relatively insignificant, but the rate of

appears to be the controlling variable with respect to wall thickness (see Fig. III-4). Two different methods were used for supplying internal heat directly to the molten salt: induction heating and electrolytic heating. Of these two methods, the electrolytically heated vessel is less complex, but corrosion of the nickel electrodes is believed to require electrode replacement on a weekly or monthly basis. The electrolytically heated vessel study has been reported in earlier Reviews,[5,6] but the inductively heated vessel tests have not. A summary of operating conditions in three inductively heated runs is given in Table III-6.

The experimental frozen-wall vessel used in the inductively heated tests is shown in a top view in Fig. III-5. It consists of an Alundum crucible, 12 in. in outside diameter by 18 in. high, with ½-in.-thick sides and bottom. The cooling coils, fabricated of ¼-in.-OD nickel tubing and spaced ½ in. apart along the vertical

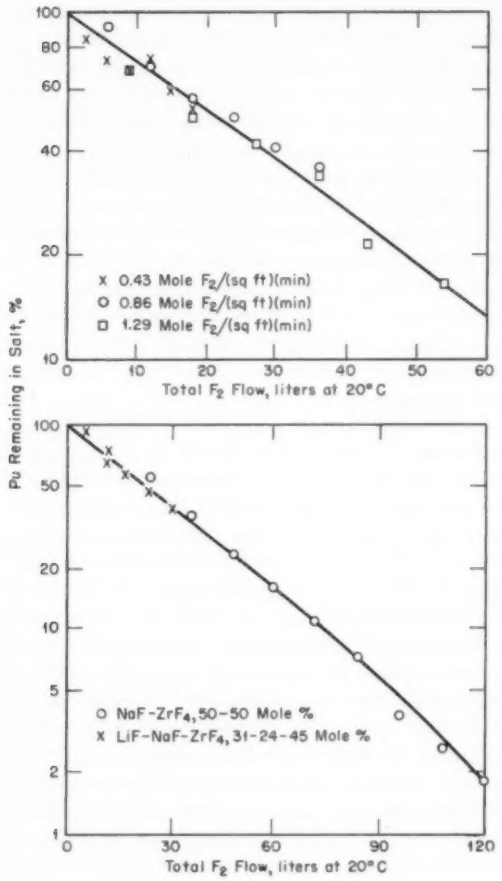
Pu Remaining in Salt, %
x 0.43 Mole F_2/(sq ft)(min)
o 0.86 Mole F_2/(sq ft)(min)
□ 1.29 Mole F_2/(sq ft)(min)
Total F_2 Flow, liters at 20°C
o NaF-ZrF_4, 50-50 Mole %
x LiF-NaF-ZrF_4, 31-24-45 Mole %
Total F_2 Flow, liters at 20°C

Fig. III-3 Plutonium hexafluoride volatilization[3] at 600°C.

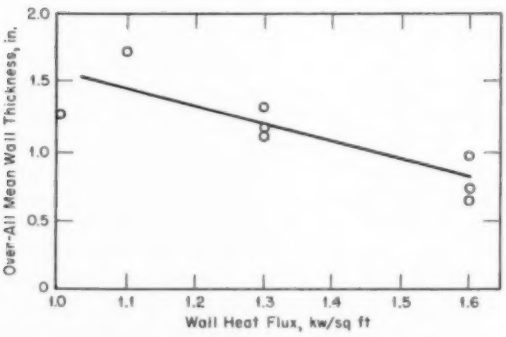

Fig. III-4 Frozen-wall thickness as a function of heat flux[4] for an electrolytically heated vessel. The salt charge was approximately 1.5 ft in diameter and 3 ft high.

Table III-6 OPERATING CONDITIONS IN FROZEN-WALL INDUCTION-HEATED TESTS[4]

(Mark I Test Assembly; Salt Is 40 mole % ZrF_4–60 mole % NaF)

	Run I-1	Run I-2	Run I-3
Plate input, kw	10.7	23.0	7.8
Salt input, kw		5.5	1.25
Efficiency, %		24	16
Wall resistance, ohms	2000		100,000
Coil turns	10	5	5
Coil length, in.	10	5	5
Coil current, r-f amp	65	125	95
Frequency, kc	350	425	415
Minimum wall thickness, in.	3/16	1/8	1/2
Bottom wall thickness, in.	3.75	1.75	1.87
Wall resistivity, ohm-cm			~10^8
Over-all average wall thickness, in.		~0.75	~1.2
Heat flux, kw/sq ft of wall		4.4	1.0

wall, are on the inside wall of the crucible. Water was used as the coolant. The stainless-steel secondary vessel is 20 in. in outside diameter by 24 in. high. The annulus between the crucible and secondary vessel is filled with tamped granules of expanded mica, which provide an electrical-insulating support for the induction coil. In Fig. III-5 the induction coil can be seen at the bottom of the annulus, which has not yet been filled with mica.

The configuration of the induction coil and of the internal cooling grid was developed for the specific purpose of this study. The desired arrangement involved the location of the cooling zone on the inside of the induction coil, being thus located between the source of electromagnetic power and the charge being heated. In this manner, close approaches of molten salt to the coil are prevented at all times. In order that the cooling means should not absorb power, it was made in the form of an array of tubes parallel to the lines of the induction field. The tubing array shown fulfilled these design requirements.

Dry Halogenation Processes

Processes Using Chlorine. A direct fluorination volatility process is being developed at Argonne National Laboratory (ANL) to recover uranium and plutonium from spent uranium dioxide fuel elements that are clad with Zircaloy or stainless steel. One concept for the

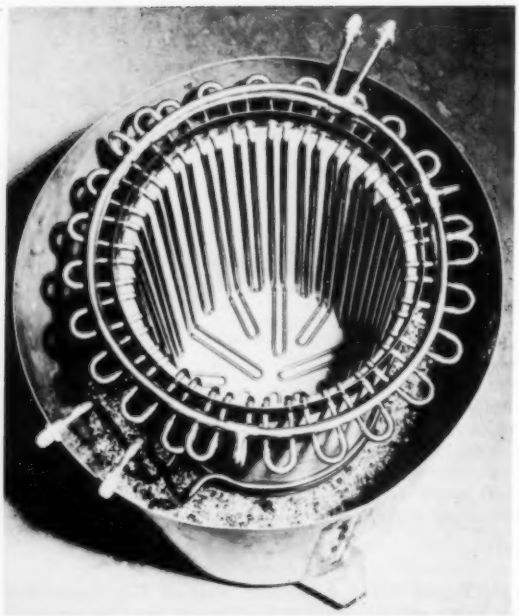

Fig. III-5 Induction-heated vessel for frozen-wall tests.[4]

decladding step of the process involves gas-metal reactions carried out with the fuel elements immersed in an inert fluidized bed that serves as a heat-transfer medium. Volatilization of the clad or alloying material by chlorination occurs in the lower zone of a two-zone fluid-bed reactor. The volatile materials pass upward into the upper zone where hydrogen fluoride is admitted to effect conversion to solid fluorides. The two zones are separated by an inverted conical baffle that reduces backmixing of the gases and prevents the formation of gas mixtures that have been shown to affect these reactions adversely. This technique has been successfully demonstrated in the case of zirconium alloy fuel[7] and has been recently applied to decladding of stainless-steel-clad fuel elements.[8]

The stainless-steel decladding process was demonstrated in a 6-in.-diameter fluid-bed reactor.[9] A 2.1-kg charge consisting of 30 tubes of type 304 stainless steel ($\frac{5}{8}$ in. in outside diameter, 31 mils in wall thickness, and 9 in. long) was placed within the reactor and supported vertically so that the tubes rested on the bubble-cap type gas-dispersion plate. The tubes, which simulated clad reactor fuel elements, were filled with Alundum particles similar to the bed material and crimped shut at both ends. The tube charge occupied 33 per cent of the reactor cross-sectional area. Anhydrous hydrogen fluoride was admitted above an inverted-cone baffle to effect the conversion of the volatile ferric chloride to solid ferric fluoride. The stainless-steel tubes were reacted at bed temperatures between 580 and 640°C with chlorine diluted to 50 vol.% with nitrogen. After 5.8 hr the stainless-steel tubes were 95 per cent reacted; this is equivalent to an average penetration rate of 5.1 mils/hr. There were no operational problems associated with this test.

Corrosion studies on nickel, Inconel, and Hastelloy C specimens aimed at preliminary evaluation of potential construction materials for the chlorination decladding of stainless-steel-clad fuels have been reported recently.[9] Tests conducted at 600°C using once-through chlorine showed an initially high but diminishing corrosion rate during the first 25 hr; a much reduced uniform corrosion rate existed during the subsequent period, which extended to 285 hr. The calculated corrosion rates were about 20 mils/month for the short term and about a factor of 10 lower for the longer term for all metals. Photomicrographs showed severe intergranular attack in nickel, no changes in Inconel, and slight intergranular changes in Hastelloy C attributed to age hardening accelerated by high temperature.

Exploratory tests indicated that above 600°C there was an appreciable reaction between chlorine and sintered uranium dioxide. A series of tests was performed[9] to investigate the nature of this reaction and identify the reaction products. Single pellets of uranium dioxide were reacted in a Vycor apparatus at 650°C using undiluted chlorine gas. In one test, approximately half of a 16-g pellet was reacted in 3 hr. It was observed that the reaction between chlorine and uranium dioxide yielded both liquid and volatile or entrainable reaction products at 650°C. The liquid product, which solidified upon cooling from 650°C, was identified by X-ray analyses to be uranyl chloride. Wet chemical analyses showed a chloride-to-uranium mole ratio of 2 for this material. The volatile constituent contained chlorine and uranium in a mole ratio of 2, but X-ray analyses showed an unidentifiable major phase. Since the reaction of chlorine and uranium dioxide

yields both liquid and volatile reaction products at temperatures above 600°C, consideration must be given to this problem in any chlorine process scheme.

In other work performed at ANL,[8] the chlorination of uranium dioxide fuel was investigated as an alternative to a direct fluorination process in the processing of ceramic oxide fuels. The concept involves the reaction between the oxide fuel and a mixture of chlorine and carbon tetrachloride in a two-zone fluid-bed reactor. The volatile uranium chlorides produced in the lower zone of the reactor are converted to solid fluorides by reaction with hydrogen fluoride in the upper zone. Several chlorinating agents were evaluated at several temperature levels, and an equimolar mixture of chlorine and carbon tetrachloride was found to give a maximum reaction rate at 550°C. A charge of 20 uranium dioxide pellets (121 g total) was 92 per cent reacted at 550°C in 2.5 hr in a $1\frac{1}{2}$-in.-diameter fluid-bed reactor. An inert bed of aluminum oxide was used to provide heat transfer and large surface area on which the uranium fluoride would deposit. An exploratory trial fluorination[9] of the uranium fluoride produced in the chlorination-hydrofluorination run showed a 96 per cent recovery of the uranium as uranium hexafluoride in 2 hr at 350°C. A major advantage of the chlorination process over a direct fluorination process is that the reagent cost for the conversion to the hexafluoride is considerably reduced, since hydrogen fluoride rather than fluorine is used for conversion to the tetrafluoride.

Processes Using Fluorine. A direct fluorination recovery process for uranium dioxide reactor fuels is under study at ANL. The dense pelleted fuel material has been shown to be capable of fluorination at a practical rate in a fluidized bed of inert magnesium fluoride particles. The bed of particles, which covers and fills the void spaces of the packed bed of oxide pellets, achieves many of the advantages of fluidization, particularly with respect to heat transfer and temperature control.

Average uranium hexafluoride production rates of about 20 kg/(hr)(sq ft of reactor cross section) have been obtained at 500°C in a 3-in.-diameter column with inert-fired pellets.[8] Approximately one-half of this rate was achieved with hydrogen-fired pellets; 10 to 12 hr was required to fluorinate a 4.5-kg batch of this material in 40 vol.% fluorine at 500°C. Two techniques of automatic temperature control have been shown to be feasible in regulation of the exothermic reaction: (1) adjustment of coolant air flow and (2) regulation of inlet fluorine flow. The latter method was observed to be faster and more positive in its action for close control at maximum reaction rates.

High fluorination rates have been obtained with oxygen-fluorine mixtures.[9] Fluorinations made with an oxygen diluent proceeded at an over-all rate from three to six times faster than with a nitrogen diluent. The oxygen evidently reacts with the pellet surface to form higher oxides that spall off as fines. The high specific surface area of these fines results in a high, nearly constant fluorination rate until the fluorination is about 90 per cent complete. The fines are retained within the equipment and are completely fluorinated without difficulty.

Since heat transfer limits the maximum practical reaction rate in the direct fluorination process, a study[8] was made in a special apparatus to measure the heat-transfer coefficients for the surfaces of an inner heater and of the outer cooling wall. Measurements were also made for determining effective thermal conductivities of systems consisting of pellet beds with a fluidized medium in the pellet voids. In several experimental tests, effective thermal conductivities along the radius of the bed were about 0.8 Btu/(hr)(sq ft)(°F/ft) for nonfluidization and were 5 to 10 Btu/(hr)(sq ft)(°F/ft) for fluidization. For the fluidized cases, surface coefficients were about 80 Btu/(hr)(sq ft)(°F) for the internal heating surface and were 20 to 60 Btu/(hr)(sq ft)(°F) for the external cooling surface.

Physical and Chemical Properties of Fluorides

Chernick et al.[10] have recently published details on the preparation of rhodium hexafluoride, part of a continuing program on the preparation of transition-metal hexafluorides being conducted at ANL. The hexafluoride was prepared by burning rhodium metal in a fluorine atmosphere in a liquid-nitrogen-cooled quartz reactor. This technique was previously used in the preparation of ruthenium hexafluoride.[7] Solid rhodium hexafluoride is black in color, whereas the gas is a deep red-brown. Rhodium hexafluoride, unlike the other transition-metal

hexafluorides, appears to decompose into fluorine and a lower fluoride at room temperature.

The heat of formation of molybdenum hexafluoride, measured by direct combination of the elements, has been reported by Settle et al.[11] to be

$$\Delta H_{f25} = -372.3 \pm 0.2 \text{ kcal/mole}$$

Data derived from these measurements are

$$\Delta S_f = -72.13 \text{ cal/(deg)(g-mole)}$$

$$\Delta F_f = -350.8 \pm 0.2 \text{ kcal/g-mole}$$

Pyrometallurgical Processing

Development of pyrometallurgical processes is being pursued at several sites in the anticipation that processing economies will result from the capability of handling short-cooled fuels with an attendant reduction of fuel inventories, from the avoidance of chemical conversions, and from the general simplicity of the processes. Development of these processes has accompanied the development of fast reactors. The high fissionable-material content of the fuels for fast reactors and the necessity of processing the fuels many times before complete fuel consumption is realized makes necessary the development of simple, economical processes for such fuels.

Melt Refining

Demonstration of several pyrometallurgical processes will be possible in the fuel-cycle facility that is being constructed adjacent to the EBR-II at the National Reactor Testing Station (NRTS) in Idaho. The first process that will be employed for the recovery and recycle of discharged fuel from this reactor is melt refining, a simple melting process in which fission-product removals are effected by volatilization and selective oxidation reactions. Construction of the fuel-cycle facility is nearly complete, and installation of equipment is expected to begin soon. Progress in the development of various equipment items (furnaces, cranes and manipulators, scrap-handling devices, crucibles, and thermocouples) is reported in the Argonne Chemical Engineering Division progress reports, the latest[12] being ANL-6413.

Recently, liquid oxide fluxes have been employed in laboratory work by the French[13] to effect selective oxidation of rare-earth and alkaline-earth elements in molten uranium and extraction into the flux. Considerable effort was expended by them in the development of phase diagrams of the very stable oxides (oxides of beryllium, lanthanum, calcium, and strontium). From these diagrams, binary and ternary combinations were found which have sufficiently low melting points for operation at practical temperatures (below 1500°C) (see Table III-7). Only mixtures involving beryllium oxide have low melting points. Oxide combinations having melting points as low as 1110°C were found.

In this work uranium oxide was employed as the oxidizing agent; thus, on reduction of its oxide by the alkaline and rare-earth elements, uranium simply replaced these elements in the molten uranium. Table III-8 shows the removal of lanthanum and barium achieved in the small-scale (50 g of uranium) laboratory studies. Re-

Table III-7 COMPOSITIONS AND MELTING POINTS OF VARIOUS OXIDE FLUXES[13]

System	Eutectic system		
	Composition, *M*	Composition, wt.%	Melting point, °C
BeO-BaO	42-58	10-90	1141
BeO-SrO	55-45	22-78	1302
BeO-CaO	58-42	38-62	1384
BeO-La_2O_3	66-34	13-87	1371
BeO-La_2O_3-BaO	41-3-56	10-7-83	1110
	60-23-17	13-66-21	1250
BeO-La_2O_3-SrO	54-3-43	20-13-67	1264
	63-32-5	13-83-4	1345
BeO-La_2O_3-CaO	53-5-42	25-32-43	1297
	65-29-6	14-83-3	1327
BeO-CaO-SrO	57-23-20	31-28-47	1215

Table III-8 REMOVAL OF SELECTED FISSION PRODUCTS FROM MOLTEN URANIUM BY OXIDE FLUXES[13]

Flux	Tracer in uranium	Liquation period at 1430°C, min	Decontamination factor
BeO-CaO-5% UO_2	380 ppm La	60	≥8000
BeO-CaO-5% UO_2	328 ppm La	15	≥8000
BeO-CaO	320 ppm La	15	60
BeO-La_2O_3	320 ppm La	15	100
BeO-CaO-5% UO_2	180 ppm Ba	15	≥1000
BeO-CaO-5% UO_2	2500 ppm Zr	60	≅0, 1*

* Evaluated from the content of zirconium in the flux.

moval of these elements was very high (≥ 1000) when uranium dioxide was used as an oxidant and still very good (of the order of 100) in the absence of an added oxidant. Zirconium was apparently not removed.

Beryllia crucibles having densities greater than 2.7 were employed in this work and were found to have good resistance to attack by the molten fluxes. Crucibles of lower density were attacked by dissolution. At the conclusion of an experiment, the uranium was removed as an intact mass by breaking the crucible. Recoveries ranged between 98.5 and 99.5 per cent. It remains to be seen whether, on a larger scale, such high yields can be effected by pouring. The larger scale work is beginning.

Fundamental Studies of Liquid-Metal and Salt Solutions

Solubilities in Liquid-Metal Systems. Knowledge of the solubilities of fissionable, fission-product, and structural elements in various liquid-metal media is required for the design of pyrometallurgical processes. Solubilities of various elements in bismuth have been reported. These include hafnium, osmium, iridium, platinum, rhenium, and cobalt,[14] magnesium and samarium,[15] and aluminum and lutetium.[1] The solubilities of scandium[1] and uranium[15] in cadmium have also been reported.

Nature and Thermodynamic Properties of Metals and Intermetallic Compounds. Phase diagrams are being developed for the solute-solvent systems of process interest to provide important basic information. Albrecht[16] at Los Alamos has investigated the plutonium-zinc system over the range of 65 to 100 at.% zinc. Four compounds ($PuZn_2$, Pu_2Zn_9, $PuZn_8$, and Pu_2Zn_{17}) were disclosed (see Fig. III-6). The liquidus was established over the range of 67 to 98.8 at.% zinc.

The phase diagram and thermodynamic properties of the thorium-zinc system have been reported by Chiotti and Gill.[17] The phase diagram in Fig. III-7 shows the existence of four intermetallic compounds having the formulas Th_2Zn, $ThZn_2$, $ThZn_4$, and Th_2Zn_{17}. Standard free energy, enthalpy, and entropy of formation for each compound were derived from vapor-pressure data.

The phase diagram of the cadmium-uranium system is shown in Fig. III-8 as reported by

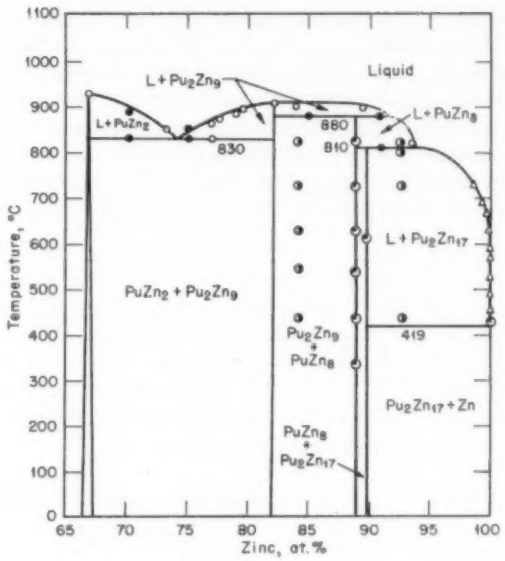

Fig. III-6 Phase diagram for the plutonium-zinc system.[16] ○, thermal-analysis data. ◔, metallographic data indicating the number of phases by the number of quadrants filled in. ▲, data from G. R. B. Elliott and R. U. Sweezer.

Martin et al.[18] The single intermetallic compound, UCd_{11}, found in this system decomposes peritectically at 473°C into alpha uranium and melt containing 2.5 wt.% uranium. Particular attention was given to establishment of the liquidus lines. Between 473 and 600°C, the liquidus line is retrograde.

At ANL a systematic study is being made of the thermodynamics of systems composed of uranium and various low-melting metals.[12] Studies of the uranium-zinc,[19] uranium-cadmium,[20] uranium-thallium,[21] and uranium-lead[22] systems have previously been reported. Currently the uranium-indium system is being investigated.[12]

Two investigations of the thermodynamic properties of uranium-bismuth alloys have been reported.[23,24] In work done at the University of Michigan,[23] the uranium solubility in bismuth over the temperature range of 400 to 800°C has been expressed as log (wt.% uranium) = 3.272 − 2690/T(°K). The thermodynamic properties of uranium-bismuth systems were determined at Ames Laboratory by measuring the vapor pressure of bismuth in equilibrium with the condensed phase using an optical absorption tech-

nique.[24] The thermodynamic activity of bismuth was measured from 725 to 875°C in the regions of U_3Bi_4 + UBi_2, UBi_2 + liquid, and the one-phase liquid region. The uranium activity was then calculated from the Gibbs-Duhem equation. The uranium-bismuth alloys were found not to be regular solutions. The activity of magnesium in dilute magnesium-cadmium alloys (0 to 1.7 wt.% magnesium) has been determined at Harwell, England, in the temperature range 440 to 560°C by galvanic cell measurements.[25]

Research is under way at Mound Laboratory to determine physical properties of various metals and alloys associated with reactor fuel systems. Among the recently published data are the density of liquid cerium[26] (Table III-9),

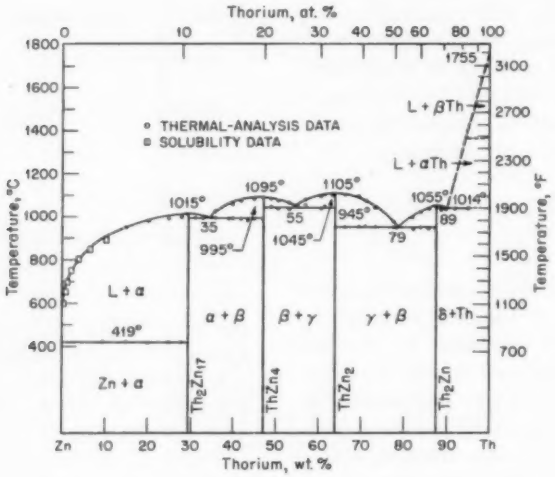

Fig. III-7 Phase diagram for the thorium-zinc system.[17]

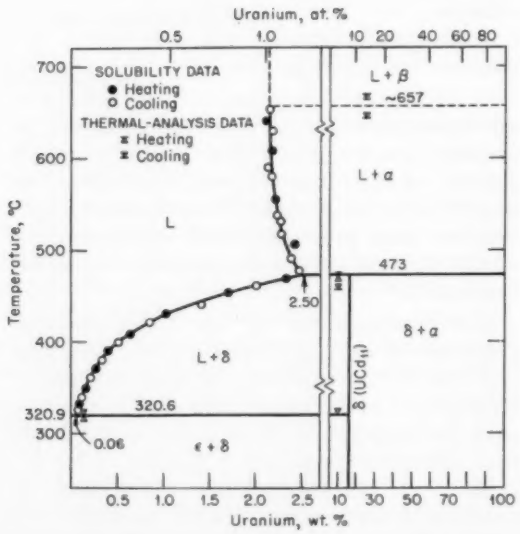

Fig. III-8 Phase diagram for the cadmium-uranium system.[18]

the viscosities of lanthanum and praseodymium[26] (Table III-10), and the viscosity of bismuth[27] (Table III-11).

Distribution of Elements Between Immiscible Phases. Studies of the distribution of fissionable and fission-product elements between immiscible liquid metals are being made in order to evaluate solvent-extraction possibilities. Distribution data recently reported by Argonne[12] for cerium and strontium in the lead-zinc system are shown in Table III-12.

Reduction of Oxides in Liquid-Metal Systems. The reduction of oxides, particularly those of uranium and plutonium, in liquid-metal systems is a step in several pyrometallurgical processes. For example, the reduction of uranium-fissium oxide mixtures by zinc–5 per cent magnesium alloys in the presence of a halide flux is a basic step in the EBR-II skull recovery process, described in the October 1961 issue of *Reactor Fuel Processing*.[28] Ex-

Table III-9 DENSITY OF LIQUID CERIUM[12]

Temp., °C	Density, g/cm³	Temp., °C	Density, g/cm³
824	6.672	903	6.675
827	6.644	906	6.663
830	6.699	955	6.640
853	6.693	990	6.628
854	6.637		

Table III-10 VISCOSITIES OF LANTHANUM AND PRASEODYMIUM[12]

Metal	Temp., °C	Viscosity, centipoises
Lanthanum	931	2.24
Lanthanum	949	2.08
Lanthanum	994	2.02
Praseodymium	968	1.2
Praseodymium	996	1.3

Table III-11 VISCOSITY OF BISMUTH[12]

Temp., °C	Density, g/cm³	Viscosity, centipoises
1003.0	9.185	0.845
925.0	9.280	0.878
804.0	9.430	0.917
706.0	9.550	1.017
595.0	9.665	1.136
541.0	9.732	1.109
476.0	9.812	1.248
289.0	10.041	1.783
279.0	10.052	1.833
277.0	10.055	1.840
267.0	10.068	1.889
262.0	10.072	1.924

periments at Argonne[12] on the reduction of U_3O_8 at 800°C in a 12 to 15 wt.% magnesium–zinc alloy indicated that the extent of reduction was limited to about 96 per cent. Magnesium concentrations of about 12 wt.% would permit a reduction in solution volume because of the high solubility of uranium (around 14 per cent solubility at 800°C as compared to 5 per cent solubility in the 5 per cent magnesium–zinc solution). However, lower magnesium concentrations of around 5 wt.% appear to be more reliable in producing complete reduction of the oxides.

In a separate study in a 5 per cent magnesium–zinc system in which the quantity of flux was increased as a variable, the reduction rate increased and the uranium loss to the flux decreased. The flux employed had a composition of 47.5 mole % calcium chloride, 47.5 mole % magnesium chloride, and 5 mole % magnesium fluoride. A sharp decrease in reduction rate occurred when the quantity of magnesium oxide by-product in the flux exceeded a certain value (11 wt.% under the particular conditions used in the experiments).

Essentially complete reduction of thorium oxide has also been achieved in a 5 per cent magnesium–zinc system in the presence of a halide flux. A study of the effect of flux composition has indicated that a minimum concentration of magnesium chloride of 30 to 35 mole % is required in a magnesium chloride–lithium chloride–5 mole % magnesium fluoride flux.

Development of Liquid-Metal and Salt Processes

Development of a liquid-metal process for reclamation of the skull material remaining in a crucible after melt refining is under way at ANL. Runs to demonstrate the process, which was described in the October 1961 issue of *Reactor Fuel Processing*,[28] continue to show adequate purification of the uranium from fission-product elements.[12] In recent runs, over 80 per cent removal of cerium, ruthenium, rhodium, palladium, zirconium, and molybdenum has been realized. The use of pressed-and-sintered beryllia crucibles (4 in. in outside diameter by 9 in. high) for retorting the uranium product from skull processing operations shows promise. Over 98 per cent of the uranium present at the retorting step was readily dumped from the crucible as a well-agglomerated mass.

Three survey runs were made to investigate the feasibility of treating stainless-steel-canned EBR-II pins by a process similar to that proposed for skull recovery.[12] Uranium pins and stainless steel were dissolved in a zinc–fused salt mixture which contained zinc chloride as a uranium oxidant. Dissolution was slow at 500°C but rapid at 600°C. Essentially all the uranium was found in the molten salt, whereas nearly all the iron and nickel remained in the zinc phase, thus making possible a good separation of these elements from uranium. Chromium, however, distributed partially (15 to 20 per cent) into the flux phase, a distribution which should be reducible by decreasing the zinc chloride concentration.

In anticipation that plutonium will be employed in future core loadings of the EBR-II reactor, the possibility of separating rare-earth fission products from plutonium through liquid-metal extraction with calcium and calcium-rich zinc solutions is undergoing investigation at Argonne.[12] The solubility of plutonium in liquid calcium at 860°C is low, about 0.10 wt.%. The distribution ratio of cerium between molten calcium and plutonium is about 0.53 on a weight basis. For a typical plutonium fuel, about 88 per cent of the cerium could be removed with approximately 0.8 per cent plutonium loss in two successive extractions at 860°C in which a calcium-to-plutonium weight ratio of 4 is used. At 860°C the solubility of plutonium in calcium was shown to increase from 0.1 to 0.7 wt.% as zinc is added from 0 to 35 wt.% zinc. The cerium distribution is not affected significantly.

Table III-12 DISTRIBUTION DATA FOR CERIUM AND STRONTIUM IN THE LEAD-ZINC SYSTEM[12]

Temp., °C	Solute	Concentration of solute in zinc layer, wt.%	Concentration of solute in lead layer, wt.%	Distribution coefficient, $K = \frac{\text{wt.\% solute in zinc phase}}{\text{wt.\% solute in lead phase}}$
652	Ce^{141}	0.14	7.6×10^{-3}	18.4
703	Ce^{141}	0.11	1.4×10^{-2}	7.9
736	Ce^{141}	0.09	1.8×10^{-2}	5.0
656	Sr^{85}	1.9×10^{-3}	2.1×10^{-2}	0.09
703	Sr^{85}	2.3×10^{-3}	2.1×10^{-2}	0.11
740	Sr^{85}	3.2×10^{-3}	2.1×10^{-2}	0.15

Pyrometallurgical processes for the separation of uranium from thorium are under study at Ames Laboratory and at Atomics International. A report on the pyrometallurgical processing of thorium-uranium fuel has been issued by Ames Laboratory.[24] A proposed process consisted of the following steps:

1. Dissolution of the fuel at 800 to 900°C to produce a magnesium–42 wt.% thorium eutectic (m.p. 582°C) and finely divided uranium precipitate.

2. Rough separation of phases at 585 to 600°C.

3. Consolidation of the uranium by addition of chromium to give low-melting 5 wt.% chromium–uranium eutectic (m.p. 860°C). This is frozen, and the magnesium-thorium solution is decanted and combined with the first magnesium-thorium supernatant solution.

4. The uranium-rich phase is then purified in a potassium chloride–lithium chloride–zinc system by oxidation-reduction reactions using zinc chloride as an oxidant and magnesium as a reductant. By these reactions, uranium is separated from chromium, molybdenum, niobium, ruthenium, and other relatively noble metals. The uranium is finally isolated as U_2Zn_{17}, which is retorted to yield uranium metal.

5. The thorium-magnesium supernatant solution is treated with a potassium chloride–lithium chloride–magnesium chloride flux to remove yttrium, rare earths, and alkali metals.

6. The solution is then placed under 1 atm of hydrogen pressure to precipitate the thorium as ThH_2.

7. The thorium hydride is separated from solution and retorted by heating at 700°C under reduced pressure to produce thorium metal.

Protactinium accompanies uranium in the above process.

The separation of uranium from metallic thorium blanket material in molten magnesium has also been investigated at Atomics International.[29] Experimental studies of the magnesium extraction of uranium from thorium-uranium alloys were brought to a close during this period. The final series of experiments involved the separation of uranium from the thorium–1 per cent uranium alloy by dissolution in molten magnesium to a 42 wt.% thorium concentration and filtration through 20-, 35-, and 65-μ porous stainless-steel filters. Recovery of thorium was accomplished by precipitation from the magnesium as the hydride, filtration of the hydride, vacuum vaporization of residual magnesium in the hydride, and decomposition of the hydride. Results were con-

sistently good, with thorium recoveries often within the range of 95 to 100 per cent of the available thorium. About 8 wt.% of the thorium remained in magnesium solution and would be recycled back to the dissolution step.

In a new method of separating uranium and thorium which was proposed by Ames, use is made of the greater tendency of uranium metal to be oxidized from a zinc solution into a chloride salt bath.[30] Both uranium and thorium can be transferred from a zinc phase to a salt phase composed of molten potassium chloride–lithium chloride eutectic by the addition of zinc chloride. Similarly, these components can be transferred from the salt phase back to the metal phase by the addition of magnesium. At 700°C the distribution of these two components between the salt and zinc can be represented by the relation $(U/Th)_{salt}/(U/Th)_{zinc} = 9.0$.

The suggested procedure under investigation for the separation of uranium from thorium is the following: reaction of the thorium-uranium alloy with zinc to form a zinc–10 to –15 per cent thorium-uranium alloy that consists largely of precipitated Th_2Zn_{17}. At 700°C the zinc phase will be liquid, and the uranium present will tend to concentrate in this phase. On the assumption that uranium is present in the original material as a minor constituent and that at 700°C the ratio of uranium to the thorium in the liquid zinc can approach a value of about 0.5, over 90 per cent of the uranium can be transferred to the salt phase to give a uranium-to-thorium ratio in the salt of about 0.7. This degree of enrichment may be suitable for some power-reactor requirements.

A literature survey on the pyrometallurgical purification of metals has been issued.[31] Sixty-three references covering reports issued between 1945 and 1960 are included.

Construction Materials

Studies are in progress at various sites to evaluate the compatibility of various materials with liquid-metal systems of the types contemplated for processing reactor fuels. Solutions of uranium in dilute magnesium-zinc alloys in contact with a molten halide flux were found to have good stability in tantalum and tungsten crucibles at investigated temperatures[12] of up to 850°C. Tungsten shows considerable promise as a container material. Several practical methods are becoming available for the fabrication of tungsten into container materials. These include pressing and sintering of powder and flame spraying and sintering.

Many binary alloys of tantalum have been tested for corrosion resistance to plutonium alloys that are being considered as fuels for the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE).[32,33] Only two elements, tungsten and yttrium, show promise of providing improvement in the corrosion resistance of tantalum.[33] Both produce a finer-grained structure with higher recrystallization temperature. In the case of yttrium, this is accompanied by an increase in the strain hardening rate. The beneficial effect of yttrium has been confirmed several times even though the element does not remain in the final metal (yttrium is removed in arc-melting or electron-beam-melting operations). Corrosion capsules are being fabricated from metal that initially contained either 0.2 per cent yttrium or 0.7 per cent tungsten.

Corrosion resistance of tantalum has improved as higher purity metal has been obtained. Oxygen and carbon are both deleterious, although carbon is tolerable at concentrations below 25 to 60 ppm. Calcium and magnesium in the fuel alloy in detectable concentrations also appear to contribute to corrosive failures. Silicon is believed to provide some protection against corrosive damage. Carbon in the fuel also appears beneficial at temperatures above 625°C.

The dissolution of zirconium-based fuel elements by molten lead chloride in the Alloy Reguline Chloride Oxidation (ARCO) process proposed by the Phillips Petroleum Company has been described in a previous Review.[34] A report of corrosion studies in the molten lead–lead chloride system has been issued.[35] Corrosion tests were run on some commercial-grade metals, an alloy steel, stainless steels, chromium-nickel, iron alloys, nickel-base alloys, cobalt-base alloys, and a chromium-nickel-cobalt-iron alloy in the system: lead–lead chloride–lead chloride vapor at 528°C under an argon atmosphere. The following metals and alloys showed a corrosion rate of 9 mils/month or less and did not suffer intergranular or other localized attack: tantalum, Incoloy 804, Hastelloy F, Carpenter-20 Cb,

stainless steels 316L and 318Cb, Haynes 25, and Haynes Multimet.

Equipment Development

Twelve distillation runs have been completed[12] in the large-scale cadmium distillation unit described in the October 1961 issue of *Reactor Fuel Processing*.[28] Distillation temperatures and rates were varied from 455 to 620°C and 12 to 67 kg/hr, respectively, with corresponding heating efficiencies of 31 to 72 per cent. In general, the unit has functioned very well. Some initial line-plugging difficulties were remedied by changes in external piping and operating procedures. Electrical-resistance liquid-level probes in the stillpot proved unsatisfactory. Thermocouples at various levels are now utilized to locate liquid levels in the stillpot.

A project has been started at Brookhaven National Laboratory to study mass transfer and mixing phenomena at 500°C in fused salt–liquid metal extraction columns. The systems to be employed are a bismuth-magnesium-zirconium-cerium metal system and a sodium chloride–potassium chloride–magnesium chloride salt system. The distributing solute is cerium. Two columns are to be employed in the study: (1) a 4-in.-ID by 42-in.-long disk and doughnut column and (2) a 2-in.-ID by 42-in.-long column packed with $\frac{1}{4}$-in. spheres.

Ultrasonic agitation has been investigated for the dissolution of thorium in mercury.[36] Laboratory-scale (7 kg) studies of thorium dissolution in boiling mercury showed dissolution rates 1500 times those realized without ultrasonic agitation. Zircaloy-2 and stainless-steel cladding materials were also eroded at low but usable rates.

Other Nonaqueous Processes

Pyrochemical processing procedures, which have been applied principally to oxide and carbide fuels, generally utilize gases, molten salts, or liquid metals as reagents and process media. The techniques and materials resemble those used in pyrometallurgical processing, and the potential economic and technological advantages of the processes are similar, i.e., a capability for handling short-cooled fuels, simplicity, and compactness. Since the fission-product decontamination provided by either type of processing is limited, remote fuel-refabrication procedures are required.

Oxide Fuel Processing

The salt-cycle process, undergoing development at Hanford in connection with the Plutonium-Recycle Program, is an electrolytic procedure for processing irradiated uranium oxide–plutonium oxide reactor fuels.[37,38] The mixed oxide fuel is dissolved in a suitable molten chloride salt by sparging the mixture with chlorine or hydrogen chloride. A portion of the uranium in solution is reduced electrolytically to the dioxide, which is essentially free of plutonium and is a by-product of the process. The plutonium and remaining uranium are then codeposited electrolytically as the dioxides. This product is thereby enriched sufficiently in plutonium that it can be recycled to the reactor after suitable makeup and refabrication steps.

The principal molten-salt systems under investigation are sodium chloride–potassium chloride, sodium chloride–magnesium chloride, potassium chloride–magnesium chloride, and potassium chloride–lead chloride. Some of the more important characteristics of a suitable salt are a practical melting point and liquid range, ease of drying, the proper chloride activity, and the formation of satisfactory uranium dioxide deposits during the electrolytic reduction.

Chemical studies of the dissolution step in molten sodium chloride–potassium chloride suggest that hydrogen chloride sparging converts the uranium oxide initially to a U(V) species that subsequently disproportionates to U(IV) and U(VI). Chronopotentiometric measurements indicate that the reducible U(VI) species in a sodium chloride–potassium chloride melt forms a reversible electrode.

Graphite and Hastelloy D have both been utilized as electrodes in the reduction step. In order to avoid conversion of the reducible U(VI) species by the graphite anode to a soluble reduced species, i.e., $UO_2Cl_2(solution) + C(solid) + Cl_2(gas) \rightarrow UCl_4(solution) + CO_2(gas)$, oxygen is included in the sparge gas.

Codeposition studies of plutonium dioxide with uranium dioxide from a sodium chloride–potassium chloride melt (uranium-plutonium ra-

tios of 10:1 and 15:1) showed the deposits to consist of mixed crystals rather than solid solutions of the oxides.[37]

An interesting technique involving time-lapse infrared photography has been employed to follow the accumulation of uranium dioxide on a cathode during the course of an electrolytic reduction. Few new crystals were formed after the first few minutes of electrolysis. Instead, the existing deposits continued to grow uniformly with little change in the surface irregularities.

Preliminary observations have been made on the oxidation state of plutonium dioxide dissolved in low-temperature melts. In potassium chloride–lead chloride (2:1) and potassium chloride–magnesium chloride, dissolution at 770°C with hydrogen chloride produced Pu(III) in solution. Elemental chlorine, however, appears to cause a partial conversion to Pu(IV).

Continued engineering investigations of the salt-cycle process on a nominal 20-liter scale have been reported.[37,38] Three preparations of uranium dioxide by electrolytic reduction of uranyl chloride from a potassium chloride–lead chloride (2.5:1) melt have been made. In the first two runs, a cylindrical graphite anode and an annular graphite cathode were used. A Hastelloy D cathode was used satisfactorily in the third run, producing a somewhat finer than usual deposit.

The dissolution step was also demonstrated on a 20-liter scale by dissolving a 25-lb charge of U_3O_8 in potassium chloride–lead chloride (2.5:1). The system was chlorinated for 8 hr at 700°C, producing a final uranium concentration of 17.0 wt.%.

Approximately 100 construction materials have been evaluated at Battelle[39] for possible use in the salt-cycle process. While corrosion tests were being made at Hanford on molten-salt systems sparged with hydrogen chloride, a parallel program was conducted at Battelle on the chlorine-sparged systems. The latter proved to be considerably more corrosive. In both programs the tests were performed at temperatures of 750 to 800°C.

No usable material with outstanding corrosion resistance toward either system was found.[39] However, a nickel-aluminum-silicon alloy appears promising on a periodic replacement basis (about three months).

The chlorination of uranium–fission-product oxide mixtures in molten-salt media has been investigated briefly at Argonne[12] as a potential modification of the liquid-metal process for the recovery of melt-refining skulls. A carbon monoxide–chlorine mixture was passed through various molten-halide systems containing about 10 wt.% uranium and fission-product oxides in suspension. The salt was stirred and held at 800 to 850°C. The following molten-halide systems were investigated:

1. NaCl (50 mole %) – KCl (50 mole %)
2. NaCl (50 mole %) – KCl (50 mole %) + Fe
3. NaCl (47.5 mole %) – KCl (47.5 mole %) – $ZnCl_2$ (5.0 mole %)
4. LiCl (47.5 mole %) – $MgCl_2$ (47.5 mole %) – MgF_2 (5.0 mole %)
5. LiCl (47.5 mole %) – $BaCl_2$ (47.5 mole %) – MgF_2 (5.0 mole %)

In salt systems 1, 2, and 3, the uranium was all in solution within 1 hr. In system 4, however, only 6 per cent was in solution after 2 hr, and in system 5 the dissolution was slow but complete after 3 hr. In system 2 the iron was added as metal, which was converted to ferric chloride. In all the melts, substantial percentages of the zirconium, molybdenum, and ruthenium were removed as volatile chlorides. In a separate group of experiments, a decrease in the dissolution rate of uranium oxide was noted when the magnesium fluoride content of a sodium chloride–potassium chloride melt was raised from 5 to 10 mole %.

The low-decontamination process being developed at Atomics International[28,29] for the recovery of highly irradiated uranium dioxide fuels employs gaseous reagents. The uranium dioxide is removed from the metallic cladding by treatment with oxygen. The dioxide is converted to U_3O_8 in the form of a fine powder. Alternate oxidation with oxygen at 200 to 600°C and reduction with hydrogen at 600°C cause a progressive reduction in particle size until the material is suitable for refabrication. Although a limited degree of fission-product decontamination results from this procedure, the primary objective of the process is to facilitate reenrichment and refabrication of the fuel for recycle.

Experiments have been performed with 100-g quantities of highly irradiated uranium dioxide.[29,40] Fuel irradiated to burnups as high

as 15,000 Mwd/metric ton of uranium has been processed. Radiochemical analysis of the material after oxidation at 275 to 300°C and reduction at 600°C shows decontamination factors of less than 3 for rare earths, strontium, ruthenium, zirconium-niobium, cerium, and cesium. Hot cave equipment is being constructed to demonstrate the complete fuel cycle, including decanning, processing, refabrication of pellets, loading of capsules, and reirradiation.

At higher temperatures it is possible to remove fission-product ruthenium from irradiated uranium dioxide by oxidation.[41] Uranium dioxide irradiated to 10^{18} nvt was exposed to oxygen at temperatures up to 1300°C. Below 600°C no ruthenium removal was observed. At 700°C one-half of the ruthenium had disappeared, and at 1300°C a decontamination factor of 25 was realized. The mechanism of removal is believed to involve the volatilization of ruthenium tetroxide. A ruthenium decontamination factor of 2.4 was obtained in five alternate oxidation-reduction cycles at 600°C.

Carbide Fuel Processing

Three potential processes for the recovery of uranium carbide fuels are being investigated at Atomics International.[29,40] One is the carbide-oxide-carbide cycle in which the carbide fuel is first converted to uranium oxide by treatment with oxygen. The carbide is then regenerated by carbothermic reduction of the oxide at high temperature. The second process scheme involves electrolytic reduction of the uranium carbide in a lithium chloride–potassium chloride bath to form dendritic uranium metal on a molybdenum cathode. The uranium deposit is dissolved in mercury. The mercury is distilled off under an atmosphere of propane which reacts with the uranium and leaves a granular residue of uranium carbide. In the third process the uranium carbide fuel is treated with nitrogen at 900°C, which converts it to a mixture of uranium nitride and carbon. The reaction is then reversed by heating to 1500°C *in vacuo*. The first and third processes offer the advantage of great simplicity; the electrolytic process, however, should result in a more efficient removal of fission products.

The carbide-oxide-carbide cycle has been demonstrated in small-scale experiments in which uranium monocarbide was oxidized, the resulting uranium oxide was reduced to the dioxide with hydrogen, and the dioxide was heated with an equivalent amount of graphite in a graphite crucible.[40] The carbothermic reduction was complete in 6½ hr at 1500 to 1600°C, producing stoichiometric uranium monocarbide (theoretical content, 4.8 wt.% carbon; analytical content, 4.78 to 4.82 wt.% carbon). A study of the reaction rates obtained in the uranium dioxide–graphite reaction showed a behavior consistent with a second-order rate equation

$$\frac{x}{1-x} = kt$$

where x is the fraction completed at time t.[29]

The oxidation of uranium carbide by oxygen, air, and water vapor has been investigated[42] at temperatures up to 600°C. The oxidation characteristics are dependent on the history of the material. The oxidation rate of freshly arc-melted uranium carbide is slow, even at 500°C, whereas "aged" material oxidizes much more rapidly. The aged or "reactive" uranium carbide ignites in oxygen at about 275°C and in air at about 350°C. The initial oxidation produces an intermediate oxide, UO_{2+x}, which is converted to U_3O_8 on further heating. For the initial oxidation, the activation energy is 7.1 kcal/mole in 10 mm of oxygen at 400 to 600°C. The oxidation rate appears to be dependent on the size of the sample. The oxidation reaction can be controlled by limiting the partial pressure of oxygen or by dilution with an inert gas.

Kinetic studies indicate that the uranium monocarbide oxidation reaction has an activation energy of 12 kcal/mole for freshly arc-melted material[29] compared to the value of 7 kcal/mole for the reactive form.[42]

Two oxidation experiments were performed with uranium monocarbide irradiated to 5000 and 15,000 Mwd/metric ton of uranium.[5] The oxidations were conducted at 270°C in air. The decontamination factors for the principal fission products were less than 3 at this low temperature.

Scaleup of the air oxidation of uranium monocarbide to U_3O_8 with kilogram quantities is in progress.[29,40] Since the reaction has a positive temperature dependence, the practical conversion rate is limited by the heat-removal capability of the equipment. The temperature is regulated by controlling the rate of air admission to the system. A rotary kiln type furnace is being considered in order to maintain the

high ratio of surface area to weight necessary to prevent temperature excursions and sintering within the solids. This equipment, with a capacity of about 10 kg, will also be used for the hydrogen reduction of U_3O_8 to uranium dioxide.

In the nitriding process for uranium carbide fuels, the reaction of uranium monocarbide with nitrogen shows some of the characteristics of the oxygen reaction.[40] Freshly arc-melted uranium monocarbide is relatively inert toward nitrogen but becomes reactive upon sufficient exposure to water vapor. The reaction of the reactive material is initiated at about 600°C and is fairly rapid at 900°C.

Work has been reported by General Atomic[43] on the reaction rates of uranium dicarbide, thorium dicarbide, and uranium-thorium dicarbide in moist air at 30 and 50°C. The reaction products were identified as uranium or thorium dioxide, hydrogen, and hydrocarbons. Both uranium dicarbide and thorium dicarbide underwent a rapid initial reaction which subsequently became very slow. The initial rates in the case of thorium dicarbide, however, were much faster than those of uranium dicarbide. The high reactivity of thorium dicarbide was not inhibited by the addition of uranium.

Possible approaches to the pyrochemical processing of carbide fuels under study at Ames[44] make use of the reactions of uranium monocarbide with molten zinc and with molten halides. When the monocarbide was heated with zinc in sealed capsules at 500 to 800°C, partial reaction occurred to form a uranium-zinc intermetallic compound and carbon. On exposure to a potassium chloride–lithium chloride–zinc chloride salt bath at 600 to 800°C, the reaction products were tentatively identified as uranium trichloride, zinc, and some undissolved carbide. Although the carbide phase was not identified positively, it is believed to be uranium dicarbide or sesquicarbide.

Several carbides and other refractory compounds of nuclear interest have been synthesized at Argonne, using volatile liquid metals as reaction media.[9] The technique shows promise for the preparation of reactor fuel materials as well as for the recovery of such fuels by pyrochemical processes.[28] The compounds prepared thus far by this method include uranium monocarbide, plutonium sesquicarbide, cerium sesquicarbide, uranium trisilicide, triuranium disilicide, and uranium diboride. X-ray diffraction and chemical analysis were used to characterize the compounds. Zinc, magnesium, and cadmium were used alone and in various combinations as the liquid-metal media. The compound is precipitated from the liquid-metal solution in which the constituents are combined. The liquid metal is then removed by an appropriate solid-liquid phase-separation technique and retorting of the solid product.

The apparent contradiction between the Ames results, in which uranium monocarbide was decomposed by zinc,[44] and the Argonne results, in which uranium monocarbide was prepared by adding carbon to a zinc solution of uranium,[12] can be resolved by a consideration of the probable equilibrium involved.[45] The solubility of uranium carbide in zinc can be represented by the equation

$$UC(\text{solid}) \rightleftharpoons U(Zn) + C(\text{graphite})$$

The solubility, i.e., concentration of uranium in the saturated liquid-metal phase, is then expressed by the equation

$$\log X_U = \frac{\Delta F_f^\circ}{2.3RT} - \log \gamma_U$$

where X_U is the atom fraction of uranium in the liquid-metal phase, γ_U is its activity coefficient, and ΔF_f° is the free energy of formation of uranium monocarbide. By using published values[46] of ΔF_f° and emf data on the zinc-uranium system,[47] the solubility of uranium monocarbide in pure zinc can be computed. The result of this computation indicates that above approximately 662°C the equilibrium solid phase is uranium monocarbide; below this temperature it is the epsilon uranium-zinc intermetallic compound (approximately $UZn_{11.5}$). Thus if equilibrium can be established for the reaction

$$UC(\text{solid}) + 11.5Zn(\text{liquid}) \rightarrow UZn_{11.5}(\text{solid}) + C(\text{graphite})$$

it should be possible to form uranium monocarbide from the elements in zinc solution above 662°C and to decompose uranium monocarbide by reaction with zinc below 662°C. Above 662°C, the solubility of uranium monocarbide in zinc computed by this method is about 0.2 at.% with a negligible temperature dependence.

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Section

IV

Reactor Fuel Processing

Waste Disposal

Evaluation of Ultimate Disposal Methods for Radioactive Wastes

ORNL has undertaken a comprehensive study to evaluate the economics and hazards associated with alternative methods for ultimate disposal of highly radioactive liquid and solid wastes.[1-5] It is expected that the study will define an optimum combination of preliminary operations and final ultimate disposal methods from the many available.

The preliminary operations to be evaluated are interim liquid storage, conversion to solids by pot calcination, interim storage of solids in pots, and shipment as either liquids or calcined solids. The ultimate disposal methods to be evaluated are storage of pot-calcined solids in salt deposits, in vaults, and in vertical shafts and storage of liquids in salt deposits, in deep wells, in the ground by hydrofracture, and in tanks.

A 6 metric ton/day plant is assumed. This plant would process 1500 metric tons of uranium converter fuel per year at a burnup of 10,000 Mwd/metric ton and 270 metric tons of thorium converter fuel per year at a burnup of 20,000 Mwd/metric ton. This hypotehtical plant would be processing all the fuel from a 15,000-Mw(e) nuclear economy, which may be in existence by 1970.

A cost study of interim liquid storage has been completed.[2] The hazards evaluation is to be made separately from the economic evaluation since it will be more qualitative. In this first report the costs of storing Purex and Thorex liquid wastes in acid and alkaline form were estimated for times of up to 30 years. The lower activity-level chemical decladding wastes were not considered in this study.

Funds for financing the interim storage facility were assumed to be allocated in a single lump sum; therefore the present-worth concept was applied for facilities not immediately needed. An interest rate of 4 per cent was assumed. Tanks designed by Savannah River were used; they were made of stainless steel for acid wastes and of mild steel for neutralized wastes. The operating cycle of each tank was assumed to consist of equal filling and emptying periods plus a full (or dead) period.

With interim storage time defined as filling time plus full time, tank costs were minimum when full time was 40 to 70 per cent of the interim storage time, using present-worth considerations. For waste-storage times of 0.5 to 30 years, costs ranged from 2.2×10^{-3} to 9.5×10^{-3} mills/kw(e)-hr for acid wastes in stainless-steel tanks and from 1.7×10^{-3} to 5.1×10^{-3} mills/kw(e)-hr for neutralized wastes in mild-steel tanks. In Fig. IV-1 the total costs of in-

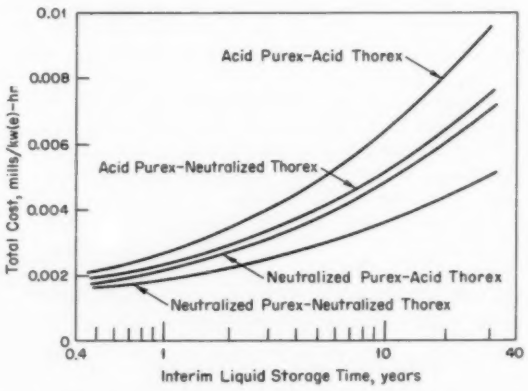

Fig. IV-1 Cost of interim liquid storage as a function of storage time for all combinations of acid and alkaline Purex and Thorex wastes.[2]

terim liquid storage, in mills per kilowatt-hour of electricity, are plotted as a function of the storage period. These costs assume that, for a given interim storage period, the optimum dead storage period is used.

A cost study of conversion to solids by pot calcination is in progress.[3,4] For seven different types of calcined solids that might be produced from wastes from the assumed 6 metric ton/day fuel-processing plant, for pot diameters from 6 to 24 in., and for interim liquid-storage times from 0.5 to 30 years before calcination, the capital costs for pot calcination varied between 1.2×10^{-3} and 2.8×10^{-3} mils/kw(e)-hr. These capital costs were estimated as a function of building size, which varies with different combinations of acid and neutralized wastes and pot diameter, and as a function of shielding wall thickness, which varies with interim liquid-storage time before calcination.

Low-Level-Activity Liquid Waste Treatment

At ORNL a scavenging ion-exchange process (Fig. IV-2) is being developed for decontaminating the large volumes of slightly contaminated water produced in nuclear installations.[1] ORNL low-level-activity liquid waste is being used for this study.

Three runs have been made in a small (60 liter/hr) pilot plant to obtain scaleup data for a 10 gal/min pilot plant being constructed to demonstrate this process.[3-6] In this process the waste solution is scavenged and filtered prior to being fed to an ion-exchange column containing CS-100, a carboxylic-phenolic resin. Feed clarification was excellent, producing an effluent with 3 ppm turbidity and 8 ppm dissolved hardness as calcium carbonate. Decontamination factors for the process were equal to or better than design specifications and confirmed laboratory-scale results: decontamination factors for strontium and cesium ≥1000; a decrease of gross β activity to 54 per cent of the MPC_w (maximum permissible concentration in water), assuming 100 per cent Sr^{90}, for 168 hr/week; and a decrease of strontium and cesium to 1 per cent or less of the MPC_w. Decontamination from cobalt and ruthenium was low. On termination of the loading cycle, the resin was eluted upflow with 10 bed volumes of 0.5*M* nitric acid. The acid eluant was then evaporated, resulting in a volume reduction of 30 to 1 without solids formation. On this basis, the over-all volume reduction factor was ≥3000.

ORNL is investigating the use of phosphates as a means of increasing strontium removal from ORNL process waste currently being treated in the Process-Waste-Water Treatment Plant.[3] This is a single-stage treatment facility employing a lime-soda softening process.[7] Phosphates would be used as a supplement to the normal treatment procedure rather than as a replacement. A dosage of 125 ppm phosphate increased strontium removal. The floc produced had better settling character than that produced by primary coagulation with phosphate, the amount of strontium removed was as much as that in the most efficient primary phosphate treatment, and careful *p*H adjustment was not required. The addition of proprietary coagulant aids greatly improved the settling characteristics of the floc.[8] During a one-week plant test, removals of Sr^{89}, Sr^{90}, and Cs^{137} increased from 79 to 87 per cent and from 85 to 97 per cent, respectively.

Natural minerals are under consideration as sorptive material for second-stage treatment of ORNL process waste.[3] Their use is predicated on their ability to sorb and retain radionuclides[6] and on the safety and economy of ultimate disposal of the contaminated solid without additional treatment. Regeneration and reuse of mineral columns would not be necessary, because of their low cost, if the total volumes of mineral required are relatively small.

To demonstrate the extent and limitation of the use of natural minerals, laboratory-scale columns are being evaluated, and a pilot plant, capable of treating up to 3 gal of treatment-plant effluent per minute, is under construction. Of a number of minerals tested, vermiculite ore is one of the most promising with respect to efficiency, availability, and cost. It is necessary to pretreat raw vermiculite and remove the readily replaceable calcium and magnesium, thus preventing their later interference with column operation. Sodium chloride is effective for this pretreatment. Distribution coefficients greater than 5000 for strontium and cesium were shown with sodium-treated vermiculite. Phosphates inhibited the rate of strontium re-

moval by vermiculite but not the rate of cesium removal.

In addition to improving the exchange capacity for strontium by a substitution of sodium for magnesium ions on the exchange complex, different methods by which sodium can be substituted for potassium in the crystal lattice in the

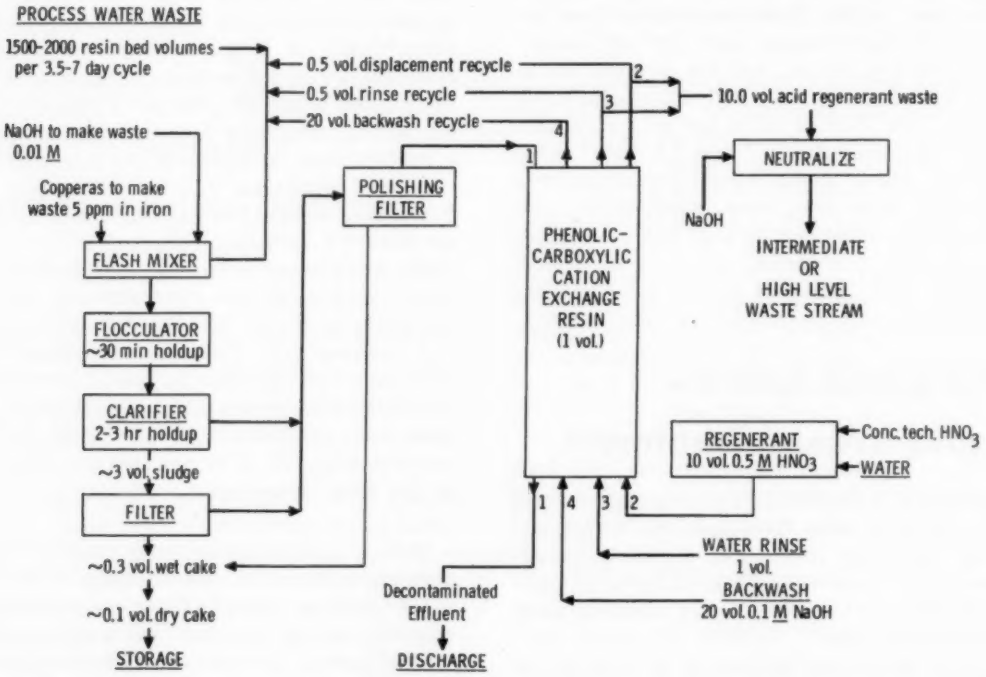

Fig. IV-2 Flow sheet for process-water decontamination with carboxylic-phenolic ion-exchange resin.[3]

biotite portion of the vermiculite (hydrobiotite) have been studied.[3] Sorption of strontium by vermiculite (after 24 hr contact) from 0.1*M* sodium nitrate solution containing strontium was increased from 20 per cent removal by natural vermiculite (*p*H 6.5) to 45 per cent by vermiculite leached with 1*M* sodium chloride (*p*H 6.5), to 70 per cent using sodium chloride–sodium hydroxide treatment (*p*H 9), and to 83 per cent after sodium tetraphenylboron treatment (*p*H 9).

Calcination of High-Level-Activity Wastes to Solids

Various calcination methods are being studied for the conversion to solids of high-level-activity wastes. Among the methods being considered are fluidized bed, radiant-heat spray, and rotary kiln. The proceedings[9] of the second AEC meeting on the fixation of radioactivity in solid media held at NRTS in Idaho[10] during September 1960 have become available. More than 30 papers were presented at this meeting, and they covered all aspects of the research on this problem. Topics discussed included all the methods of calcination, as well as fixation in glass and ceramics, ion exchange, and the associated problems of off-gas cleaning, construction materials, and characteristics of solids and final disposal.

Hanford has continued its investigation of three calcination processes for the treatment of Purex plant type liquid wastes—unagitated batch or pot, radiant-heat spray, and fluidized bed.[11–13] Among the newer approaches to the problem of fixation of high-level-activity wastes is a Hanford concept in which the processes of radiant-heat spray calcination and pot calcination might be combined advantageously.[13] The former would evaporate the waste and calcine the solids at a relatively low temperature, thus

probably minimizing fission-product evolution. The latter would carry the calcination to final stages, would allow considerable flexibility with regard to the addition of fluxes as needed, and would provide increased control of smaller-volume off-gas streams. Plans are under way for building an experimental spray calciner–pot calciner combination capable of processing full-level radioactive waste.

An ORNL pot-calcination unit and a BNL rotary calciner are to be designed and installed in a waste-calcination pilot plant at the ICPP.[3,5,14] The pilot plant is intended to demonstrate the calcination of Purex, Thorex, Darex, or TBP-25 wastes at average batch rates of 5 gal/hr, to a final calcination temperature[3,5] of 900°C. The pot and rotary calciners would be operated with common auxiliary process and mechanical handling equipment. The equipment could ultimately be used to demonstrate the fixation of wastes in phosphate glasses. Space will be provided in the facility for storage of the calcination pots or rotary-calciner powder receivers for one year to permit observation of temperature, pressure, and vessel integrity prior to final disposal.

A design summary and cost estimate of the pilot plant prepared by ORNL[14] indicates an initial cost of $1 million for purchase and installation of equipment in existing cells at the ICPP hot pilot plant at Idaho. A cost of $1.5 million was estimated for construction of a new building for installation of this equipment at ORNL. Preliminary design of the pilot plant is scheduled to start in January 1962, and equipment installation at the ICPP should begin by January 1963.

Pot Calcination

In calcination studies of simulated Purex high-level waste solutions by the unagitated batch process, emphasis was placed on extending data on calcine melt formation as a function of waste-solution composition.[12,13] Melt formation is of interest because calcines that melt generally have higher densities and thermal conductivities which are desirable properties for radioactive waste in long-term storage.

Purex high-level wastes can vary considerably in chemical composition because of Purex-process variations and changes, and because of the various process steps the primary waste may or may not undergo prior to calcination. The principal waste constituents are sodium, iron and aluminum sulfates, and nitrates. Any or all of the minor constituents (chromium, nickel, lead, potassium, phosphate, acetate, silica, manganese dioxide, and fission products) will also be present in the waste solution. Alkaline wastes will also contain sodium hydroxide and perhaps sodium carbonate.

In general, in order to form a melt below 900°C, the sodium-to-metal ion (iron, aluminum, chromium, nickel) mole ratio must be between 1.1 and 8, and the sulfate-to-salt nitrate (total nitrate minus hydrogen ion) mole ratio must be greater[12] than 1. At increasing sodium-to-metal ion ratios, the sulfate-to-salt nitrate ratio must be increased if the calcine is to become molten at temperatures of 900°C or less.

A poorly defined relation has been observed between sodium sulfate content of the mixture and its melting or consolidation to a dense compact body at temperatures[13] in the neighborhood of 900°C. Although the sodium sulfate content should largely determine the behavior of the system, such factors as oxide particle size and shape, size and shape of agglomerates, viscosity, surface tension, gas generation, temperature gradients, heating rate, and other unspecified effects all seem to enter in to determine how the mixture will consolidate. Mixtures of iron and sodium sulfate exhibited a minimum melting point in the vicinity of 700°C and a sodium-to-iron ratio of 6 to 1. The melt was very fluid. Mixtures of aluminum and sodium sulfate behaved similarly as did a complex mixture representing the Purex waste. However, the sulfates of those compounds decompose below 900°C with the evolution of sulfur dioxide and oxygen and the separation of refractory oxides such as ferric oxide (Fe_2O_3), resulting in two undesirable effects in the pot-calcination process: pressure buildup in a sealed container, and buildup of a load of recirculating sulfuric acid in the liquid streams that would not have a ready exit from the process.

The relative concentrations of iron, aluminum, and chromium were studied to determine their effect on calcine melting.[13] A difference in melting behavior was observed for the five runs. Only the calcine obtained from the solutions with the iron-to-aluminum ratio of 1.5 melted completely. All the other calcines exhibited partial melting in varying degrees. The

generation of internal pressures was evident in several of the runs.

Internal pressures also developed when a simulated waste solution had a sulfate-to-salt nitrate ratio of 1.4, a sodium-to-metal ion ratio of 8.0, and no minor constituents.[12] The sulfate concentration was slightly greater than the stoichiometric sodium equivalent. During the calcination step, molten solids erupted from the pot. In a repeat of this run with 40 per cent more solution added to the pot, the solids did not erupt but rose as a plug out of the pot. Sectioning of the cooled pots revealed a dense, impervious layer above highly porous solids. It is postulated that the iron and aluminum sulfates in the bottom layer started to decompose at about 700°C. The decomposition gases were unable to escape through the impervious cover layer. No internal pressure buildup was observed in another experiment, in which the same cation concentrations were present as in the runs that developed internal pressures but in which the sulfate concentration was reduced to slightly less than the stoichiometric equivalent of the sodium concentration.

Annular-shaped containers are being investigated at Hanford for the storage of calcined radioactive wastes.[13] The annular container shape provides a large surface area per unit volume of calcined wastes which allows the fission-product decay heat to be dissipated safely and at the same time reduces the number of containers needed. The annular pot used in the bench-scale studies is illustrated in Fig. IV-3. The disengaging section is used for phase separation during boildown and for "storage" of deposited solids prior to meltdown. Upon melting, this calcine volume is further reduced by one-third to one-half. A general heat-transfer equation has also been developed relating temperatures in right circular cylindrical and right circular cylindrical annulus containers full of high-activity-level calcined waste with other parameters of vessel size, heat-generation rates, coolant temperatures, calcine thermal conductivity, and vessel-to-coolant heat-transfer rates.[13]

Five bench-scale batch-calcination-process runs were made in annular pots so as (1) to determine the feasibility of induction heating, (2) to study foaming during solution boildown, and (3) to investigate methods of removing the calcine from the pots. With induction heating,

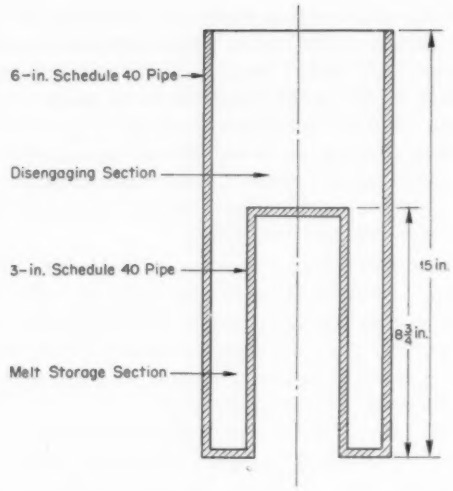

Fig. IV-3 Annular-shaped container for storage of calcined wastes.[13] The construction material is type 304L stainless steel.

the heat is generated in the calciner pot wall, and a heat source operating at a temperature higher than the terminal container temperature is not required. The faster heatup and cooldown times obtainable with induction heating should shorten the time cycle. The response of boilup rates to changes in energy input should also be faster. No operating problems were encountered that could be attributed to the use of the annular pot geometry or to the use of induction heating. The calcine melted as expected in all the studies.

To study foaming during the boildown step, two runs were made with a waste of the same relative compositions but at different concentrations. Severe foaming was observed in the first run. The second run, in which the solution was 42 per cent more concentrated, did not give a serious foaming problem. The boiloff rate in the latter was three times that measured in the run that foamed. Foaming of simulated waste solutions high in phosphate was controlled in the annular pots by the tangential introduction of air into the boiling solution so that a mild swirling action was produced. Foaming appears to become less of a problem as the pot diameter is increased, being a great deal less in 6-in.-diameter than in 3-in.-diameter pots.

A summary of the ORNL laboratory- and engineering-scale pot-calcination studies for

the period September 1960 to June 1961 can be found in the annual progress report for the Chemical Technology Division.[5] This work has been covered in previous Reviews.[1] ORNL has issued two topical reports on the pot-calcination process which are of interest—a recapitulation by Hancher[15] of preliminary scouting experiments and a summary by Godbee and Roberts[16] of laboratory developments of this process.

Spray Calcination

Allemann and Johnson at Hanford have summarized the more than 130 spray-calcination runs made with simulated waste-feed solutions in the laboratory-scale reactor.[17] Mathematical treatments of radiant-heat transfer to droplets and of particle and gas temperature during particle ignition and calcination are contained in the appendixes of their topical report.

The spray calcination of simulated wastes has been studied at 800 to 900°C in a relatively small-scale reactor 8 in. in diameter and 10 ft in length.[17] A wide variety of compositions have been handled without difficulty, and these include Purex wastes (both acidic and neutralized), TBP-25, Darex, and Zirflex. For the control of density and powder-product characteristics, sugar and phosphoric acid were sometimes added to the aqueous feed. Corrosion evaluations indicated that, in the calcination of Purex waste, sugar and phosphate additives increased the corrosiveness of the medium. Of several alloys tested, only Inconel looked reasonably good when additives were present, but stainless-steel type 446 exhibited a low corrosion rate when the additives were not used. Inconel and stainless-steel type 446 formed very stable and strongly adherent oxide films.

A continuous spray calcination with a meltdown experiment was recently carried out in the radiant-heat spray calciner.[12] A stainless-steel receptacle heated to 800°C was attached to the bottom of the filter section for receiving and melting the calcined powder blown off the calciner filters. For this run, 30 liters of simulated acidic Purex waste was fed to the calciner at 10 liters/hr. The calcined powder fell without difficulty into the pot after being blown off the filters. The melt volume was 1.6 liters, which is about $^1/_{18}$ of the original feed volume, and the melt density was 3.0 g/cm^3. The pot showed no evidence of corrosion. Analysis of the product showed 0.19 per cent nitrate and 61.4 per cent sulfate.

If a spray calciner or other continuous drying device is used, continuous conversion of the solid to melt is desirable.[13] The above work has shown that a consolidated solid could be continuously formed directly in a heated container. However, the characteristics of the solid, or paste at high temperature, are such that they could not be melted in a furnace at 900 to 1000°C and then discharged into a container. By modifying the composition with anion additives, such as sulfate, phosphate, or borate, fluid melts can be obtained. By requiring that the container walls be at high temperature only during the period of filling, corrosion should be reduced. A fluid melt, introduced directly, should result in a continuous body with good heat-transfer properties, thus allowing more complete filling of the storage container since no allowance would have to be made for foaming during evaporation and drying. Phosphate was shown experimentally to be the additive of choice.[13] With it, a considerable range of cation compositions can be brought to fluid melts at 900°C or less. The melts are sufficiently fluid to flow readily into the container and to fill it uniformly. Boric acid additions result in much more viscous melts.

A newly designed filter section was installed on the spray calciner.[13] It replaced the filter arrangement[18] consisting of eight tubular elements with automatic air-pulse blowback which had been in use for a year. Excessive pressure drop due to a successive buildup of hard-caked powder on the surface of the filter elements necessitated replacement[11] of the filter section. As in the previous design, the blowback principle is used.

The filter section was fitted with high-temperature cloth filters made of aluminum silicate Fiberfrax cloth. The cloth is a rough tweedy material with stainless-steel wire interwoven for added strength. The purpose of the cloth filter is to provide a flexible backing for the powder filter cake. The cloth bulges during blowback and causes the cake to chip off. During 10 hr of running with blowback, the pressure drop for three cloth filter elements with a total area of 4 sq ft stayed at or below 1 in. Hg at 3 ft/min filter velocity.

Back-flushing with water or with water and air was found to be very effective in cleaning Purex waste powders from rigid filter elements

that could not be blown off with the short air pulse. The method restores the elements to like-new condition. Water flushing is also effective in decontaminating cloth filters, but it has an adverse effect on the deentrainment capabilities.

For either pot or spray calcination of Purex type wastes, the volume of noncondensable off-gases was shown to be essentially the same and is the order of 10 to 100 times the feed volumes for Purex wastes.[12] These off-gas volumes are very small by gas-handling standards. For instance, at a feed rate of 100 gal/hr, the 22.2 cu ft of off-gas produced per minute in the worst case could be handled by a CWS filter of about 1-sq ft area.

Fluid-Bed Calcination

Loeding and associates[19] at ANL have summarized the feasibility and demonstration program[20] completed there on the fluid-bed calcination of ICPP-produced aluminum nitrate-bearing wastes and Hanford Purex-process wastes. This report covers pilot-plant runs made in 3- and 6-in.-diameter calciners with active and inactive synthetic feed solutions.

The work at ANL was undertaken as a part of a parallel program with the ICPP to apply the calcination technique to the specific aluminum nitrate-bearing wastes produced at the ICPP. ANL was to cover mechanical operability and to study the behavior of fission products using radioactive feed solutions. The ICPP was to study factors such as equipment scaleup, particle-size behavior, and particulate removal from the off-gas using inactive feed solutions.

Following the completion of these experimental studies, ANL then conducted exploratory studies in the existing equipment for the calcination of Hanford Purex-process wastes. The ANL program was to be concerned primarily with the feasibility and general operability aspects of the process. The behavior of fission products and the cleanup of the off-gas stream were of secondary interest, inasmuch as these problems had already been investigated for ICPP waste. Hanford was then to continue these studies, undertaking a developmental program in a new, slightly larger unit.

Runs were made in the Hanford fluid calciner to investigate the porous-plate type of fluidizing-gas distributor and the addition of sugar to feed solutions as a means of accelerating nitrate decomposition.[12] Simulated Purex high-activity-level waste feeds and the extended-tip feed nozzle[10] were used in these studies. The standard bubble-cap fluidizing-gas distributor plate was replaced with a porous plate consisting of a double-thickness layer of heavy vitreous silica cloth. Comparison of the two types of distributors, under comparable conditions, shows that the porous-plate type of fluidizing-gas distributor is preferable to the bubble-cap type with the Hanford calciner design and feed composition, primarily because of improved fluidization and decreased attrition of the calcine bed.

Although the addition of sugar (to a final concentration of 130 g/liter of original feed—high acid type) offers the advantages of additional heat supply (due to the exothermic reactions between the sugar and the nitrate) and decreased agglomerate formation rate, these advantages are more than offset by the large increase in fines formation (to about 11 per cent of the total calcine) and the more frangible and less dense calcine (1.3 vs. 1.5).

At the ICPP, test-stand studies have been made of a pneumatic, two-fluid, external-mixing, atomizing nozzle to be used in the ICPP Demonstrational Waste Calcining Facility.[1,21] The atomization characteristics of the spray and the performance characteristics (flow rates, pressures) of the nozzle when spraying into air were determined using feed solutions composed of either water or aluminum nitrate. Feed rates from 10 to 50 gal/hr and nozzle air-to-feed volumetric ratios from 300 to 1100 were investigated.

The results have shown excellent atomization of water in air at nozzle air-to-feed volumetric ratios greater than 500. Changes in nozzle performance were shown to be caused by nozzle physical effects, such as erosion and installation techniques, as well as by feed-solution composition effects. The air flow rate of the nozzle was found to be a direct function of the air supply-to-discharge absolute pressure ratio and to be predictable by theoretical methods. Changes in nozzle performance found during these studies indicate that the control of feed rates based simply on nozzle-performance calibration is inadequate. It was recommended that feed nozzles should be thoroughly tested in a pilot-plant calciner to determine the effects of nozzle variables on calciner operation and that nozzles should be calibrated in place in the

demonstrational calciner before the calciner is operated.

Vitro has summarized the results of its research for the ICPP on calcined-waste storage.[22,23] In this study, fundamental information was obtained on the physical and chemical properties of fission-product oxides and nitrates (ruthenium, cesium, cerium, strontium, niobium, and zirconium), the thermal stability of selected fission-product oxides and nitrates at temperatures up to 1500°C, and the gas-phase decomposition of ruthenium tetroxide.

The Massachusetts Institute of Technology (MIT) has been studying the conversion of high-level-activity wastes into a stable solid, such as vitreous fusions (fused glasses), as an effective and safe means of permanent disposal.[1] If the fused glasses are stored in an underground vault, a major problem of cooling would arise from a continuous generation of heat within the glass from decaying radioisotopes.[24] A study of the cooling of these fused glasses shows that free convection cooling with air offers a possible safe and economical solution to this problem. For vertical slabs of glass, about 5 in. thick and 4 ft high, containing about 30 wt.% of waste oxides, free-convection cooling with ambient air is possible when a channel of about 1 in. width is provided between the slabs.

Adsorption on Natural Materials

At Hanford the mineral bed fixation of fission products from various plant wastes[11] continues to be investigated, using samples of actual Hanford plant effluents as well as synthetic solutions.[12,13] Components in the plant wastes which are not normally included in synthetic waste formulations have a significant effect on the results of these studies, emphasizing the importance of conducting experiments with actual wastes. Anomalous results have arisen from the influence of unanticipated minor components, such as suspended silt, organic materials, and ammonium ion.

Clinoptilolite is being evaluated in the laboratory for the removal of fission products from sodium salts in the supernatant solution of neutralized Purex high-level-activity waste,[12] its use in this application being suggested by the high cesium content of this supernatant solution and by the selectivity of clinoptilolite for cesium. The column effluents containing most of the inert salts could either be discharged to the ground or treated by processes designed for handling decladding wastes. The mineral bed could be either dried and stored as a radioactive solid or eluted. The eluate from such a bed would be suitable feed for a high-level-waste calcination process or could be returned to underground tanks for storage with considerable reduction in the stored volume.

In elution studies of cesium from clinoptilolite with solutions of sodium nitrate, ammonium nitrate, ammonium hydroxide, and ammonium sulfate, the ammonium nitrate was most effective, a 10*N* solution eluting more than 97 per cent of the cesium in two column volumes,[12] and a 2*N* solution eluting 98 per cent of the cesium in six column volumes.[13] Approximately twice as much volume of ammonium sulfate solution was required to attain the same elution as with ammonium nitrate. Cesium elution was very slow with 2*N* nitric acid. The *p*H of 5*N* solutions of ammonium nitrate, ammonium sulfate, and ammonium acetate, in the range from 1 to 4, was shown to have little effect on the elution of Cs^{137} from clinoptilolite.[13]

Radiostrontium was also rapidly eluted from clinoptilolite by ammonium nitrate or sulfate solutions; more than 99 per cent is removed in the first column volume.[13] Previous experiments have indicated that incomplete elution of strontium from a bed of clinoptilolite was due to an apatite lattice formed from calcite impurity in the mineral and phosphate in the waste.[13] Treating the clinoptilolite with acid to remove calcite prior to column experiments with neutralized waste results in strontium adsorption and elution curves of the conventional type.

Clinoptilolite was found to be effective for the fixation of all fission products in neutralized Purex-waste supernatant solution except ruthenium. Its removal on beds of metal turnings is being examined.[11,12] The removal of ruthenium, cerium, and zirconium-niobium from neutral solutions with beds of iron or lead granules was found to be dependent on the formation of oxides on the surface of these metals. To utilize successfully a bed of metal granules for waste decontamination, it is necessary to retain those oxides in the bed. Iron grain sizes above 0.7 mm were not effective in retaining

iron oxide. Beds of iron granules with a grain size of 0.71 to 0.83 mm removed about 70 per cent of the radioactive ruthenium, cerium, and zirconium-niobium from a 0.01*M* sodium nitrate solution spiked with Purex waste solution; beds of 0.35 to 0.50 mm iron grain size removed more than 95 per cent of these fission products from solution.

For metal beds of small grain size, the reaction occurs mainly in a narrow zone in which oxide formation may cause rapid plugging of the bed. Mixing the iron granules with an inactive material was found to be effective for preventing such plugging. A mixed bed of iron granules and limestone chips removed more than 90 per cent of the radioactive ruthenium, cerium, and zirconium-niobium from 1270 bed volumes of the test solution (*p*H of 5) at a flow rate of a about 400 ml/(cm^2)(hr).

Experiments[12,13] in the Micro Pilot Plant at Hanford were continued to evaluate clinoptilolite for decontaminating Purex tank-farm condensate.[11] In one experiment about 2800 liters of waste solution at a temperature of 25°C was processed,[12] the waste feed containing the following isotopes in concentrations greater than their MPC$_w$: Sr^{89}, Sr^{90}, Cs^{137}, Ru^{106}, Zr^{95}, Nb^{95}, and Ce^{144}. The *p*H of the feed dropped from 9.5 to 8.8 during the run. The waste was first passed through a column of activated carbon to remove emulsified and soluble organic impurities. The effluent from the carbon column was passed through two 1-in.-diameter by 20-in.-long columns of clinoptilolite in series at a flow rate of 16 ml/(cm^2)(min). The particle size of the clinoptilolite was about 0.9 to 1.1 mm in the first column and about 0.5 to 0.9 mm in the second column. Both fractions were pretreated with 5 per cent sodium hydroxide solutions and vigorously washed to remove clay associated with the crude mine-run material.

Cesium-137, although not removed by the carbon treatment, was removed with a decontamination factor of about 750 at the start of the run, decreasing to about 350 when the second clinoptilolite column became plugged and had to be valved out after treating 1425 liters of waste. The plugging of the second column was attributed to particles in the waste. At the start of the last half of the run, cesium was removed by the remaining column of clinoptilolite with a decontamination factor of 100, which decreased to 14 by the end of the run. If the MPC$_w$ of Cs^{137} is considered as the breakthrough point, the coarse material was effective in removing cesium from 1800 liters or about 7200 column volumes of the waste. Although both the carbon and the clinoptilolite removed strontium (an over-all decontamination factor of 20 to 80), the Sr^{90} in the effluent exceeded its MPC$_w$ during most of the run. The addition of 100 ppm phosphate to the clinoptilolite feed during part of the run did not noticeably change the decontamination factor for cesium or strontium. The carbon treatment partially removed zirconium, niobium, and ruthenium isotopes, but the clinoptilolite removed essentially none of these isotopes.

In another run, strontium removal using the calcite-phosphate reaction was studied.[13] About 2600 liters of Purex tank-farm condensate waste at a temperature of 40°C was passed first through a column of activated carbon and then, in series, through a column of clinoptilolite and a column of calcite. The carbon column was effective in removing strontium with a decontamination factor of 4 to 10. The decontamination factor across the clinoptilolite and calcite columns was about 10 to 15 when no chemicals were added or when only 200 ppm sodium hydroxide was added. When 100 ppm phosphate ion was added along with the sodium hydroxide, the decontamination factor reached a maximum of 20. Even during the early part of the run, the Sr^{90} in the effluent exceeded the MPC$_w$ by a factor of 2.

Cesium-137 removal was accomplished effectively by ion exchange with the clinoptilolite. The addition of sodium hydroxide and trisodium phosphate for the calcite-phosphate rearrangement reaction did not alter the initial efficiency for removing Cs^{137}, but the capacity for removing the isotope, using MPC$_w$ as the breakthrough point, was only 5800 column volumes. This compares to the 7200 column volumes obtained when only phosphate was added during a short period in the run described above.

Concentrations of ammonia as high as 0.013*M* were measured in samples of Purex boiling-waste-tank condensate.[13] Although ammonium salts are not normally used in the Purex process, some fission-product recovery wastes containing about 0.8*M* ammonium ion were recently added to the waste storage tanks. About half the condensate is recycled back to the waste tanks; thus significant time is required to clear the ammonia from the system. Its

presence explains many difficulties encountered in trying to obtain the expected cesium capacities of various ion-exchange materials.

Suspended organic material in Purex boiling-waste-tank condensate was more effectively adsorbed by a bed of activated carbon when the solution *p*H was below 5 than at the normal solution[13] *p*H 9. Although the carbon bed did not remove all dissolved organic material, the effluent was free of suspended matter. A bed of activated carbon removed suspended organic material from about 1500 bed volumes of acidified Purex boiling-waste-tank condensate before breakthrough. Tests using simulated condensate wastes showed that the presence of soluble TBP and hydrocarbons had little or no effect on the cesium decontamination ability of clinoptilolite.[12]

Final Disposal into Salt Formations

ORNL has issued its third status report[25] on waste disposal in natural salt formations[1] which covers the period from February 1959 to September 1961. The first status report[26] defined the waste-disposal problem in a nuclear power economy, discussed the availability and nature of salt deposits in the United States, and outlined the anticipated problems of disposal into natural salt formations. The second status report[27] presented the results of laboratory experiments and theoretical calculations of the mechanism and rate of heat dissipation through rock salt. In addition, the design of proposed field-scale experiments was presented. The third report presents the results of work on model experiments with salt blocks in the laboratory, small field tests in the Hutchinson Mine of the Carey Salt Company, two large experiments in the Carey mine (Fig. IV-4), and studies of the interaction of Purex waste with salt. The model experiments were used in developing the design of field experiments, and the small-scale field experiments were operated to determine the effects of impurities in the salt and to "shake down" the equipment and operating procedures for the larger tests.[3]

The major problems of radioactive liquid waste disposal in natural salt formations have been defined as those related to the combined effects of pressure, temperature, radiation, and chemical interaction on the structural properties of salt and the control of reactive and radioactive gases that may emanate from the wastes.[3,25]

Preliminary studies have indicated that the effects of radiation on the structural properties of rock salt are minor.[25] Theoretical studies have shown that the temperature of radioactive liquid wastes stored in salt cavities can be kept within acceptable limits by controlling the age of the wastes and the size of the cavity. Heat-transfer rates measured in the field experiments agree very well with computations on which the experiments were based. Further analytical studies of the thermal problems associated with disposal of wastes in salt show that a cooling period of at least three years before ultimate disposal is desirable because of the rapid decrease of maximum temperatures with increased cooling times out to about 1000 days.

Laboratory studies have shown that the production of nitrosyl chloride (NOCl), hydrogen chloride, and nitrogen oxides produced by chemical action in salt-saturated, acid Purex waste could be controlled by maintaining acid strength below 4*M* and/or temperature below 60°C. There was no significant difference in gaseous reaction products from experiments in pure salt and in a part of the structure containing significant quantities of anhydrite. Radiolytic gas product in the salt-acid Purex waste system can be controlled by suspending the waste solutions as surface films on crushed salt or by fixing them as absorbed water in the lattices of certain minerals.

Synthetic, neutralized and acid (7*M*) Purex type wastes were used in the field tests. These wastes were assumed to come from natural or slightly enriched uranium fuel irradiated to 10,000 Mwd/metric ton at a specific power of 33 Mw/ton and processed to produce 800 gal of waste per ton. The fission-product heating was simulated by impressing an a-c voltage across graphite electrodes inserted into the synthetic waste solution and then varying the power to correspond to a predetermined fission-product decay function.

The acid-waste experiment was terminated after 197 days of operation, and the neutralized-waste experiment was terminated after 392 days.[3] In each case, temperatures were allowed to fall naturally until the waste and the surrounding salt temperatures returned to ambi-

ent, about 100 days. After the solutions reached ambient temperature, the wastes were removed from the large test cavities for disposal.

Measurements and photographs of the walls of both cavities were compared with those taken before the cavities were filled. In the acid-waste cavity there is little undercutting at the liquid level. The surfaces of the cavity walls below the liquid level are pitted with pockets 4 to 6 in. deep. Most of the damage seems to have occurred below the liquid level. Salt is deposited on the bottom to a depth of about 1 ft. In the neutralized-waste cavity there is a deep (~16 in.) undercut of the shale at the elevation of the vapor-liquid interface. The walls are covered with a heavy layer of recrystallized salt, and a layer of recrystallized salt also covers the sludge at the bottom, and a shelf of recrystallized salt extends 12 to 15 in. out from the wall just above the liquid level.

Measurements of plastic flow around the test cavities in the Carey mine were made. In the center of the room, the rate of movement prior to startup was 0.0005 in./day; when the power was cut off 400 days later, the rate of movement was 0.004 in./day. The total floor-to-ceiling movement for the duration of the heating cycle was 0.65 in., about 0.50 in. more than would have occurred normally.

A salt-disposal operation was examined which was to be capable of handling the ultimate storage of waste from a plant processing all the fuel from the projected (1970) thermal capacity (33,000 Mw) of power-generating reactors in the United States.[25] This plant would process 3.3 tons of fuel per day, and the 200 gal of waste thus produced per day would be cooled in tanks for eight years before disposal in salt. At this time the specific power would be 8 watts/gal or 1600 watts/one-day batch. An ambient

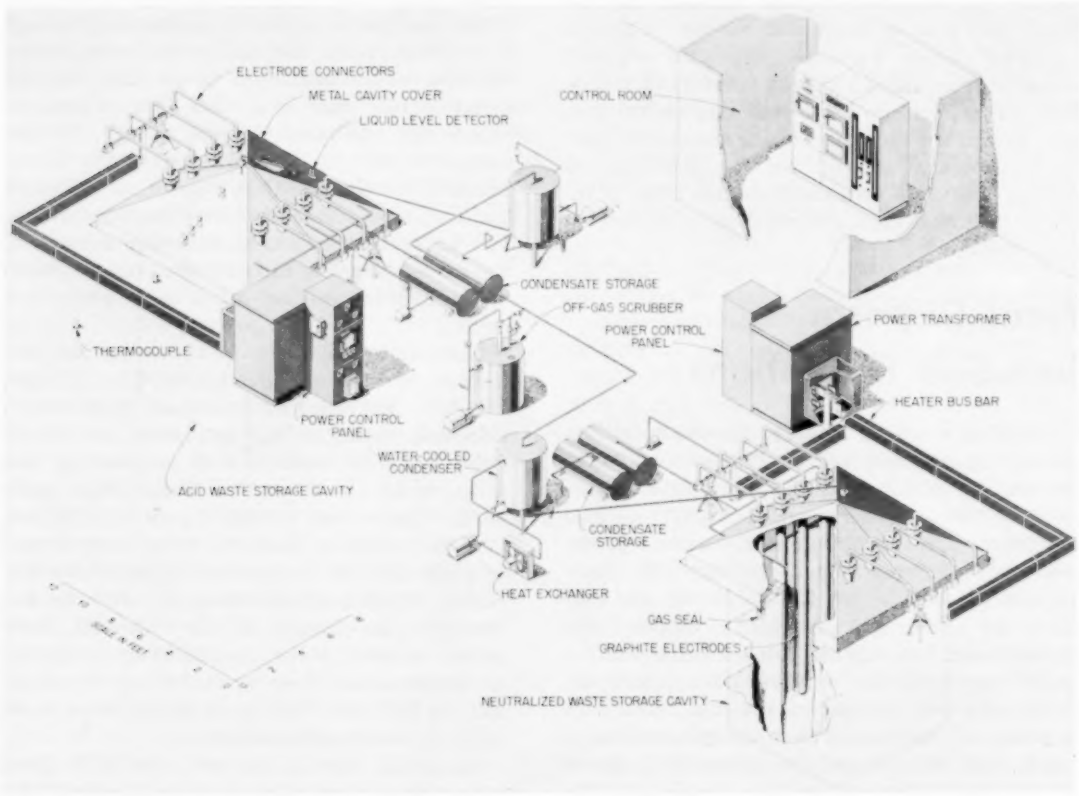

Fig. IV-4 AEC-ORNL waste-disposal field test, Carey Salt Company, Hutchinson Mine.[25]

salt temperature of 70°F and a 125°F rise in waste temperature were assumed.

Table IV-1 is a tabulation of calculations showing the effect of waste age and dilution on sphere size and the number of cavities required per month for storage. It is obvious from this table that it would not be practical to dispose of large batches of short-cooled wastes from this plant in a single sphere by diluting them to the extent required to limit the temperature rise to 125°F. For wastes cooled as long as eight years, it might be feasible to dilute and contain as much as a one-month batch in a single sphere (74 ft in diameter), although it seems likely that the 16 small spheres ($4\frac{1}{2}$ ft in diameter) would be more economical.

Table IV-1 EFFECTS OF WASTE AGE AND DILUTION ON ALLOWABLE SPHERE SIZE AND NUMBER OF CAVITIES REQUIRED PER MONTH[25]

Waste age, years	Heat-generation rate, watts/gal	Dilution factor (*N*)	Volume of sphere,* gal	Diameter of sphere, ft	No. of spheres per month
8	8	1	3.7×10^2	$4\frac{1}{2}$	16
		10	1.2×10^4	$14\frac{1}{2}$	5.2
		10^2	3.7×10^5	45	1.6
		5×10^2	4.1×10^6	101	0.7
3	18	1	1.1×10^3	3	56
		10	3.4×10^5	$9\frac{1}{2}$	19
		10^2	1.1×10^6	30	5.6
		10^3	3.4×10^6	95	1.9
		10^4	1.1×10^8	300	0.6
0.25	260	1	2.0	0.8	3000
		10	6.2×10^1	$2\frac{1}{2}$	970
		10^2	2.0×10^3	8	300
		10^3	6.2×10^4	25	97
		10^4	2.0×10^6	80	30
		10^5	6.2×10^7	250	9.7
		10^6	2.0×10^9	800	3
		10^7	6.2×10^{10}	2500	1

*Sphere which will achieve a steady-state temperature rise of 125°F when filled with a fluid having a constant heat-generation rate equal to the value listed in column 2 divided by the dilution factor.

It thus appears that, for storage of the projected high-specific-activity wastes, numerous closely spaced cavities would be required. In fact, from the standpoint of economics and heat transfer, the best configuration for salt-mine disposal of large quantities of long-cooled high-level liquid waste would seem to be a single horizontal layer of waste. An infinite slab calculation for 200 gal of eight-year-cooled wastes per day having a heat-generation rate of 8 watts/gal indicates that 575 sq ft of storage area will be required for one day's plant output;[25] or for one year's output, a gross mine area of about 10 acres.[3]

Separation of Specific Isotopes

ORNL has been developing a solvent-extraction flow sheet[10] for the recovery of fission products from Purex wastes—strontium and rare earths by extraction with D2EHPA (di-2-ethylhexyl phosphoric acid) plus TBP in Amsco, and cesium by sodium tetraphenylboron in hexone.[5]

In the recovery of strontium, a four-cycle flow sheet, previously studied, has been revised to a three-cycle flow sheet.[5] In the first cycle the strontium and rare earths are extracted and separated from iron; in the second cycle the rare earths and the strontium are partitioned, and the rare earths are recovered; and in the third cycle the strontium is recovered. In laboratory tests with nonradioactive solutions, the chemical and physical operability of the new flow sheet was excellent, with no emulsions or precipitates being formed in any cycle. In the first cycle of a continuous run made in mixer-settler equipment, about 5 per cent of the iron

impurity in the feed was extracted, but only 0.02 per cent was stripped into the first-cycle product, giving a separation factor from iron of 4.4×10^3. In the second cycle, 98.2 per cent of the rare earths was recovered as product. Separation factors were: rare earths from sodium, 9×10^3; rare earths from iron, 1.3×10^2. Strontium in the rare-earth product was below the level of analytical detection. The rare earths were concentrated by a factor of 30. In the third cycle, essentially 100 per cent of the strontium was recovered and concentrated by a factor of 30. The separation factor for strontium-iron was 100, and that for strontium-sodium was 130.

In other work at ORNL, solvent extraction has been used by McHenry and Posey[28] for producing high-purity Sr^{90} (separating from calcium) and by Butler and Ketchen[29] for separating Y^{91} and Ce^{144} from the gross rare-earth fission-product fraction.

In laboratory experiments, cesium was extracted from Purex waste, adjusted to *p*H 5, by $Na(C_6H_5)_4B$ (sodium tetraphenylboron) in hexone and stripped with dilute acid.[5] The contact with acid converts the $Na(C_6H_5)_4B$ to a form that does not extract cesium, and the solvent therefore cannot be recycled. Without an extractant recycle, a satisfactory process might be devised if the organic phase could be loaded to about 1 g of cesium per liter of 0.3*M* $Na(C_6H_5)_4B$ in hexone and if the chemical could be obtained commercially at about $5 per pound. In studies thus far the organic solubility of the cesium has been limited to 0.3 g/liter of 0.3*M* $Na(C_6H_5)_4B$, currently a specialty chemical, whose price ranges from $50 to $180 per pound. Other diluents and diluent additives are being studied for the possibility of increasing the solubility of the cesium complex in the organic phase. A stripping method is also being sought that will not destroy the cesium-extraction ability of the compound.

In the Hanford program for the recovery and purification of fission products from Purex plant wastes, flow sheets have been developed which employ ion-exchange and solvent-extraction processes.[30–32]

The purification of multicurie quantities of Sr^{90} is being done in the Hot Semiworks facility at Hanford. Two runs were made, each employing a different flow sheet. The first flow sheet consisted of a solvent-extraction cycle followed by an ion-exchange cycle.[30] The flow sheet approximated the conditions of the study flow sheet described in a previous Review,[8] with these significant exceptions:

1. About 40 per cent of the solvent-extraction product was back cycled to the feed (at a volume percentage in the feed of 4 per cent or less).
2. Citric acid (1*M*) at a *p*H of 2.7 to 3.0 was used as the ion-exchange scrub.
3. Sodium nitrate (4*M*) was used as the primary elutriant. This elution was stopped when 80 per cent of the strontium had been eluted. The remaining strontium was eluted with 0.1*M* EDTA (ethylene diamine tetraacetic acid) at a *p*H of 8.0.

With this flow sheet, about 84 per cent of the Sr^{90} processed was recovered; an additional 15 per cent, tailings from elution of the ion-exchange column, was stored for recycle in the second run. The decontamination performance exceeded the required product specifications by at least twofold for both radiochemical and inert (calcium plus barium) impurities.

The second flow sheet consisted of two cycles of solvent extraction,[31] utilizing the solvent-extraction cycle of the first flow sheet. Citric acid (1*M*) and dilute nitric acid were used as the first- and second-cycle stripping solutions, respectively. Approximately 91 per cent of the Sr^{90} processed was recovered, the remaining 9 per cent being lost to the first- and second-cycle waste streams. The product met all specifications except for Ce^{144} contamination, which was about sevenfold high. This was attributed to a feed-pump failure and to the necessity of processing and collecting the second-cycle product in equipment used for the first-cycle operations.

In the laboratory a number of batch contact studies relating to the development of the flow sheets for the recovery of Sr^{90} were made.[30–32] Highlight results of these studies are summarized below.

1. Recycling the solvent-extraction product solution to the feed stream (to obtain additional concentration of strontium) at volume ratios as high as one part product to eight parts feed can be done without adversely affecting extraction-column operation.[30]
2. Wash-procedure data for the removal of residual radioactive constituents from Hot Semiworks solvent indicate that the solvent can

be cleaned up adequately either for disposal or for sustained recycle.[31,32]

3. Either HEDTA (*N*-hydroxyl ethylene diamine triacetic acid) solution or sodium acetate–EDTA solution was indicated to be superior to citric acid as a wash solution for removing cerium from the Hot Semiworks ion-exchange column following a loading of the column.[30] These reagents do not complex strontium at the higher *p*H's as strongly as does citrate.

4. A study of the precipitation of strontium carbonate from a citrate product solution has shown that 98 per cent of the strontium can be precipitated with sodium bicarbonate.[15] The precipitation of cerium prior to the precipitation of strontium carbonate has demonstrated that cerium decontamination factors of 20 to 50 are readily obtained.[31] Cerium hydroxide can be precipitated without appreciable loss of strontium at *p*H below 12 with the addition of a small amount of Fe(III) or inert cerium to provide a carrier precipitate. The precipitate is readily filterable on filter paper.

The alkaline supernatant in the tank-stored Purex waste at Hanford[30–32] provides a potential source of Cs^{137}. Precipitation, solvent-extraction, and ion-exchange techniques are being examined in the development of a flow sheet for its recovery.

Sodium tetraphenylboron was indicated to be an acceptable reagent for precipitation of cesium from tank-farm supernatants and from cesium crude cuts.[30] Excellent cesium recovery can be obtained over a wide range of temperatures, *p*H, and digestion times. Most common anions had virtually no effect, at least at concentrations up to 1*M*. The presence of sodium nitrite and sodium nitrate did not affect cesium precipitation appreciably at high *p*H. Phase separation could be made equally well by either filtration or centrifugation. Only iron, even when complexed with tartrate, is highly deleterious.

Sodium tetraphenylboron was also used in solvent-extraction studies and was found to give appreciable extraction, being extremely dependent on the diluent used. At a sodium tetraphenylboron concentration of 0.05*M*, the cesium distribution coefficients were 0.06, 3, and 39 for hexone, amyl acetate, and nitrobenzene, respectively. The extraction increased with about the 1.5 power of the sodium tetraphenylboron concentration. Cesium was readily back extracted from amyl acetate solution with 0.1*M* nitric acid, whereas over 0.5*M* was required from nitrobenzene. Phase separation was also poor with the nitrobenzene system. A number of other diluents yielded relatively high cesium-extraction coefficients.

The recovery of Pm^{147} from Purex-plant crude-cut solution is also under consideration at Hanford.[32] A solvent-extraction flow sheet is being developed to recover a rare-earth fraction free of cerium and strontium which would then be suitable for ion-exchange processing to separate promethium from the other rare earths. A flow sheet under consideration involves: (1) extracting cerium, promethium (as representative of noncerium rare earths), calcium, and barium into D2EHPA; (2) removing strontium from the organic phase by partition; (3) stripping cerium, promethium, and calcium from the organic with 1*M* to 2*M* nitric acid; and (4) oxidizing cerium to Ce(IV) and extracting the Ce(IV) into an organic phase. The aqueous phase could then be used without further treatment for ion-exchange treatment or subjected to another extraction-stripping cycle to recover promethium in a more suitable solution.

Because a pressure buildup had been experienced in an Sr^{90} shipment to ORNL, Hanford has been investigating the feasibility of shipping the casks loaded with strontium in a "dry" condition, i.e., with most of the interstitial liquid siphoned out.[1,30] This would have the dual advantages of increasing the void volume in which gas can collect (from about 1 gal to 6 gal) and at the same time reduce the rate of gas production. To determine the effect of self-heating on the elution characteristics of the adsorption media used in the shipments, samples of Decalso (an inorganic silicate ion-exchange material) loaded with strontium were heated to simulate the worst possible conditions expected during shipment and then eluted with 4*M* ammonium nitrate. The maximum temperature which would be achieved in dry shipment with an air atmosphere was calculated to be 86°C. The laboratory data indicated that dry shipment is satisfactory, provided that a heated elutriant (80°C) is used for strontium desorption. A strontium recovery of 94 per cent was achieved. Experiments are also under way at Hanford to define the maximum shipping temperature which would still permit elution, since this temperature would define the capacity of the Hanford

(HAPO-IA) shipping cask.[32] Prior Hanford and Oak Ridge experiments show that 100°C is acceptable but that strontium cannot be eluted after heating to 400°C.

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, Plutonium, and Their Compounds

Uranium Dioxide Production

The Naval Reactors Branch of AEC has issued a handbook[1] on uranium dioxide which is a complete coverage of present technology on the production of uranium dioxide for power reactors. The handbook includes completely referenced material on uranium dioxide production and fabrication, physical properties, uranium-oxygen systems, solid-state reactions, oxidation and corrosion, and irradiation effects.

Electrolytic Reduction of Uranyl Chloride

The process of electrodepositing coarse crystalline uranium dioxide from a fused-chloride electrolyte has been studied for application to the recovery of uranium dioxide from spent oxide fuel elements,[2] the preparation of large single crystals of uranium dioxide,[3] and the production of uranium from ore concentrates.[4] Each of these applications is based on the fact that crystalline uranium dioxide can be prepared by the reduction of uranyl chloride contained in a sodium chloride–potassium chloride eutectic.

A pilot plant for the production of electrolytic uranium dioxide has been described by Chalkley.[4] The electrolyte is prepared by the direct chlorination of uranium oxides with chlorine gas in a melt of sodium chloride–potassium chloride eutectic at 800°C. Uranium dioxide, U_3O_8, and uranium trioxide are all suitable feed materials. The uranyl chloride product dissolves in the melt probably through the formation of double chlorides $K_2(UO_2)Cl_4$ and $Na_2(UO_2)Cl_4$. Silica pots have been found satisfactory as chlorination reactors in pilot-plant demonstration tests. Chlorine is passed into the melt through a silica tube leading to the bottom of the pot, and the oxide is added at an even rate to the surface of the melt. Chlorine efficiencies of up to 70 per cent have been observed. The chlorination of uranium ore concentrate proceeds as rapidly as with pure uranium oxide. Due to the physical nature of the oxide, chlorination of recycled electrolytic uranium dioxide is difficult, and prior roasting to U_3O_8 is recommended. Melts containing about 20 wt.% uranium dioxide (as uranyl chloride) have been found most suitable for electrodeposition.

The electrolytic reduction of uranyl chloride is carried out between graphite electrodes at a potential of 1 to 3 volts and a cell temperature of 800°C. Uranyl ions are discharged at the cathode, and chlorine is liberated at the anode. The reaction at the anode is complicated by the formation of uranium tetrachloride by the carbon reduction of uranyl chloride in the presence of chlorine. The production of uranium tetrachloride tends to produce erosion of the uranium dioxide product, resulting in a low cathode efficiency. Also, the concentration of uranyl chloride in the melt is lowered, causing an increase in the cell resistance and limiting the yield of uranium dioxide obtainable in a single electrolysis. There are, however, certain advantages of the presence of uranium tetrachloride in the melt. If the concentration of uranium tetrachloride is allowed to increase, the bath is maintained in a reduced state; and, under these conditions, a uranium dioxide product of low oxygen content ($UO_{2.0}$ to $UO_{2.05}$) and high density (>10.8) is produced. Without this reducing action, an oxide of higher oxygen content is formed. The anodic reaction may be used to dissolve additional oxide during the electrolysis.

A single-stage electrodeposition process can be used to produce electrolytic uranium dioxide crystals from a melt formed by chlorinating uranium ore concentrate, but three stages are

required to achieve high-purity crystals. The first electrolytic stage removes the bulk of both soluble and insoluble impurities from the uranium values. The starting melt for the first stage is prepared from melt recycled from the second electrolysis cell and contains about 20 wt.% uranium dioxide as uranyl chloride. The electrolysis is carried out at 30 amp with an applied voltage of 1.1 to 1.8 volts. The uranium dioxide deposits are collected and leached in 1 per cent hydrochloric acid. Nine electrolyses are made before purification of the electrolyte is required to remove accumulated impurities. The rate of ore concentrate addition to the melt is adjusted during the final electrolysis to leave the final melt with a sufficiently low content for the uranium to be recovered by simple aqueous leaching.

The partially purified uranium dioxide is dissolved in the sodium chloride–potassium chloride eutectic for further purification in the second stage. The cell is operated at an applied voltage of 2 volts. A third electrolytic step is employed to complete the purification cycle. The third cell is operated under slightly reducing conditions to prepare oxide of low oxygen content and to ensure minimum deposition of rare earths with the uranium dioxide.

The electrolytic uranium dioxide produced from ore concentrates was a crystalline material with crystals primarily larger than 100 mesh. The impurity levels of thorium, potassium, and sodium in the third-stage product ranged from 100 to 200 ppm each. The concentration of individual rare-earth metals was less than 10 ppm. The carbon content of the electrolytic oxide was high (500 ppm); this level of contamination could be reduced by careful control of the method whereby the deposits are separated from the cathodes.

The electrolytic deposition of uranium dioxide from a fused-chloride electrolyte is also being applied to the processing of spent oxide fuel elements. This work is discussed in Sec. III of this issue.

Conversion of Uranium Hexafluoride to Uranium Dioxide

A two-step fluid-bed process for the preparation of high-density uranium dioxide from uranium hexafluoride is currently being studied at ANL.[5] Uranium hexafluoride is reacted with steam at 225°C to form uranyl fluoride in a fluid-bed reactor. Uranyl fluoride is then reduced to uranium dioxide with a steam-hydrogen mixture. The problem of fines formation and particle-size control encountered in previous work[6] was solved by allowing the fines to be entrained from the reactor and collected in a separate filter chamber. With the use of a proper seed-particle recycle rate, particle growth during extended operation was avoided. A 1-in.-diameter pipe was used to transport the fines from the fluid-bed reactor to the filter chamber. Uranyl fluoride product was withdrawn intermittently from the bottom of the reactor. Since the modification of the unit, good control of the bed particle size has been maintained in runs up to 15-hr duration. Seed-particle addition at 14 per cent of the uranium hexafluoride feed rate maintained the average particle size at approximately 315 μ. The maximum value for the −200-mesh fraction in the bed was held to 0.2 per cent. These results indicate that the fines formation problem can be avoided by control of the bed particle size using the entrainment-separation technique for preventing accumulation of fines in the bed.

A problem encountered in this series of tests[5] was the accumulation of uranyl fluoride deposits on solid surfaces above the fluidized bed. This deposition of uranyl fluoride has been extensive in several tests, and development work is being directed toward correcting this behavior.

The reduction of uranyl fluoride to uranium dioxide has been studied in batch fluidization runs in a 3-in.-diameter reactor.[5] In a 4-hr run at a bed temperature of 650°C, an optimum gas mixture of 50 per cent steam in hydrogen gave a residual fluoride content of 200 ppm in the uranium dioxide product. Considerably higher residual fluoride content was obtained at a bed temperature of 550°C. Appreciable particle breakup was observed with the formation of 36 wt.% −200-mesh particles. This particle behavior may not be of process significance if the uranium dioxide product is used directly in the manufacture of pellets.

Workers at the Oak Ridge Gaseous Diffusion Plant are also investigating a two-step fluid-bed process for the conversion of uranium hexafluoride to uranium dioxide.[7] A primary interest in this process is the recovery of hydrogen fluoride from depleted uranium hexafluoride. The pilot-plant equipment (see Fig. V-1) consists of an 8-in.-diameter fluid-bed reactor, in which uranium hexafluoride is converted to

uranyl fluoride with steam, and a 6-in.-diameter fluid-bed unit in which uranyl fluoride is reduced with hydrogen and steam to form uranium dioxide. Both reactors are equipped with agitators to provide a stirred fluidized-bed system. Uranium hexafluoride and steam are metered separately to the 8-in. reactor, and the uranyl fluoride product overflows continuously with the outlet gases into the uranyl fluoride feed hopper.

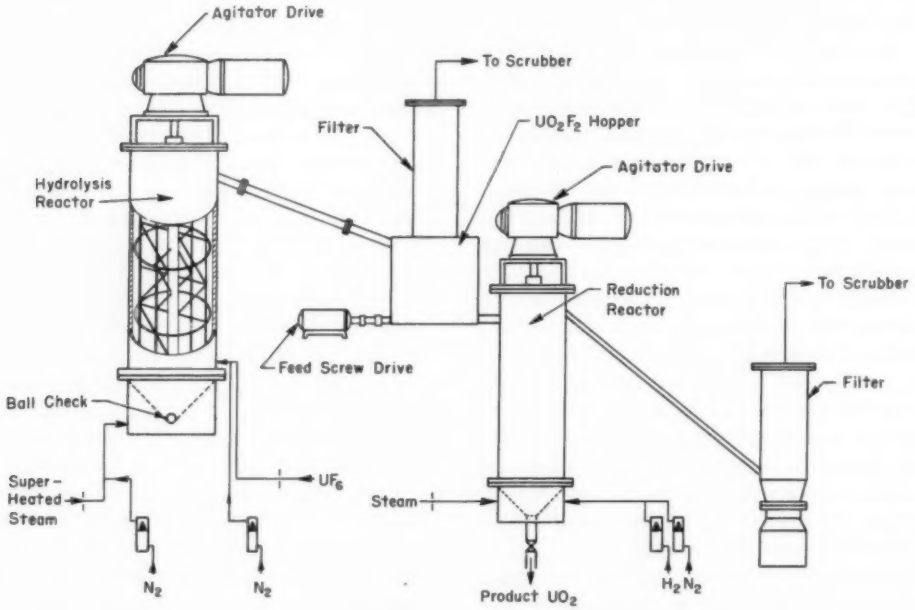

Fig. V-1 Pilot plant for conversion of uranium hexafluoride to uranium dioxide.[7]

Experience has indicated that it is possible to recover efficiently approximately 98 per cent of the fluoride as hydrogen fluoride in the two-step fluid-bed process. It has been observed, as in similar experience at ANL, that proper particle-size control was critical in the fluid-bed conversion of uranium hexafluoride to uranyl fluoride and that accumulation of uranyl fluoride deposits on solid surfaces introduced many operational problems.

Oxidation of Uranium Dioxide

The uranium-oxygen system is one of the most complex of the metal oxide systems. The existence of at least four thermodynamically stable uranium oxides (UO_2, U_4O_9, U_3O_8, and UO_3) has been definitely proved, and several additional oxides have been reported. The system is further complicated by polymorphism, solid solution, and metastability phenomena. Thus the mechanism of the preparation of uranium dioxide by hydrogen reduction of uranium trioxide or intermediate oxides is not readily elucidated in this complex system, nor are the mechanisms governing oxidation processes.

Published information on the oxidation of uranium dioxide and intermediate oxides includes that by Hoekstra et al.[8,9] of ANL and by Sudo and Kigoshi.[10] The oxidation and reduction equilibria of the composition range of UO_2-U_3O_8 have been measured[10] at 360 to 580°C. The authors suggest that two regions are in the composition range of UO_2-U_4O_9: a homogeneous region, in which oxygen dissolves in uranium dioxide, and a heterogeneous region of uranium dioxide saturated with oxygen and U_4O_9. The composition range of U_4O_9-U_3O_8 was observed to be a homogeneous solid solution. These results are at slight variance with the published data of Hoekstra et al.,[8] who suggest the existence of intermediate phases containing a $UO_{2.3}$ species in the composition range of U_4O_9-U_3O_8. A tentative phase diagram (Fig. V-2) of the system UO_2-U_3O_8 was compiled by Hoekstra et al.[8] from

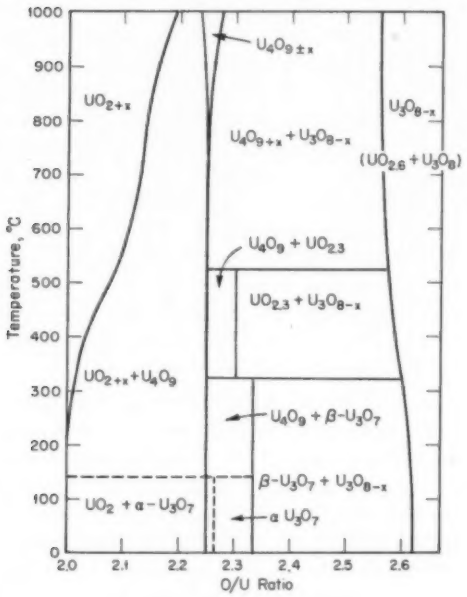

Fig. V-2 Tentative phase diagram[8] of the system UO_2-U_3O_8.

data based on the results of several investigators. In the system U_3O_8-UO_3, an intermediate phase, $UO_{2.9}$, is reported to be stable between 520 and 610°C and to have a structure[9] similar to U_3O_8. This material is olive green in color and possesses an orthorhombic structure. Comprehensive data on the uranium-oxygen system are given in reference 1.

Preparation of Uranium Carbides and Other Refractory Materials

In the preparation of uranium monocarbide by the reaction between uranium metal and hydrocarbons, propane has shown greater reactivity than methane. The kinetics of the reaction between propane and uranium hydride were investigated in a flow system.[11] The optimum conditions for forming uranium monocarbide containing 4.8 wt.% carbon were selected as ½ hr of carburizing time at 600°C. At similar temperature conditions, the reaction rate with methane is too slow to be practical.[12] The carbide product from the propane reaction frequently contained low-density flakes of pyrolytic carbon. Tests[13] showed that these pyrolytic carbon deposits did not occur as readily on the surface of the reactor or support members when constructed of copper rather than Inconel or stainless steel. The use of copper inserts in the reactor completely eliminated the presence of carbon flakes in the carbide product but did not affect the free carbon content of the uranium monocarbide.

A principal difficulty in the design of a nuclear reactor employing uranium carbide as the fuel material is the reactivity of the fuel with moisture to form oxide. A process was developed at Battelle Memorial Institute (BMI) whereby the carbide fuel in powdered granular form would be coated with a protective pyrolytic carbon film. Oxley et al.[14] have published data on the kinetics of carbon deposition in fluidized beds of uranium dioxide, uranium monocarbide, and uranium dicarbide. The evaluation of the properties of the carbon coatings was primarily based on the ability of the coatings to protect the fertile material against attack by hot concentrated nitric acid for periods of 8 hr. These leaching data indicated that a 7-μ coating deposited by pyrolysis of acetylene at 1015°C on uranium dioxide provided good protection. However, a 7-μ coating deposited from methane at 1125°C on uranium dicarbide powder did not provide adequate protection. It was determined that a 9-μ layer on uranium monocarbide, a 17-μ coating on uranium dicarbide, and a 30-μ deposit on thorium-uranium dicarbide were within the safe coating-thickness region.

Sylvania-Corning Nuclear Corporation[15,16] has been investigating a process for producing uranium monocarbide directly from uranium hexafluoride by reduction with silicon metal in the presence of carbon. Initial trials indicated that the reaction at 1150°C terminated with the production of a uranium tetrafluoride intermediate. Further reduction to uranium carbide was possible only if the molten uranium tetrafluoride were retained in the reaction zone. Presently, studies are being directed toward the preparation of uranium monocarbide by the reaction of uranium tetrafluoride with silicon and carbon.[16] Variable quality uranium monocarbide was prepared in initial tests at 1625 to 1750°C; the product contained up to 1 per cent each of silicon, oxygen, and nitrogen impurities.

Methods for synthesizing various uranium ceramic compounds have been published. Taylor

and McMurtry[17] describe several methods for preparing uranium monocarbide, uranium mononitride, and uranium silicide (U_3Si_2). Each of these materials has inherent advantages over uranium dioxide to warrant consideration of their use as reactor fuels if economic production techniques can be developed. Eding and Carr[18] have prepared a variety of high-purity binary uranium compounds. Procedures were developed for preparing uranium compounds with boron, carbon, nitrogen, selenium, silicon, and sulfur. In most of these systems several different stoichiometric compounds were prepared in high purity.

Uranium Metal Preparation

Reduction of Uranium Oxides

Workers at Eldorado Mining and Refining, Ltd.,[19] have developed a method for producing uranium-aluminum alloys by the direct reduction of uranium oxides with aluminum in the presence of cryolite (Na_3AlF_6). The oxide is blended with 40-mesh size aluminum powder and cryolite and is heated in a graphite crucible under a layer of cryolite for 20 min at 1400°C. The proportions of reactants found best for slag-metal separation and melt uniformity were six times stoichiometric aluminum for uranium dioxide reduction and four times stoichiometric aluminum for U_3O_8 reduction. Good phase separation was obtained when a quantity of cryolite was added to produce a slag containing 16 wt.% aluminum oxide and 84 wt.% cryolite. Alloys of uranium and aluminum have been prepared with compositions up to 68.8 wt.% uranium. Uranium metal yields of greater than 95 per cent have been consistently obtained from the alloys.

Experiments have also been performed[19] on the reduction of sodium and magnesium diuranates with aluminum. High alloy yield and good phase separation were obtained by using four times stoichiometric aluminum as the reducing agent.

The possibility of using a magnesium-zinc alloy in a continuous pyrometallurgical process for the production of uranium metal from the oxide has been investigated by Hewitt[20] at Harwell. The effects of magnesium-zinc alloy composition and stirring rate on the reduction reaction were studied at 800°C. It was observed that the reaction of uranium dioxide with stoichiometric alloy was extremely slow; but, as the concentration of magnesium was increased, the rate of reaction passed through a maximum. Highest reduction efficiencies were obtained with an alloy containing 6 wt.% magnesium; about half the oxide was reduced in 2 hr at 800°C using this alloy composition. The effect of stirring rate on the reaction rate was inconclusive. It was concluded that even under the most optimum conditions the reaction seems to be too slow and incomplete to be of practical value in the production of uranium metal.

Workers at ANL have found that U_3O_8 may be rapidly and quantitatively reduced to uranium metal with a zinc–5 wt.% magnesium alloy at 750°C in the presence of an alkali or alkaline-earth chloride flux. A comparison[21] of a variety of fluxes indicated that fluxes composed entirely of group II cations gave complete reductions. Rapid and complete reductions were also obtained with a flux containing 47.5 mole% lithium chloride, 47.5 mole% magnesium chloride, and 5 mole% magnesium fluoride. In experiments in which complete reduction was achieved within 30 min, magnesium chloride was present as a major component of the flux (47.5 mole %). Therefore magnesium chloride may be considered to be an essential ingredient of any flux chosen for effective reduction of uranium oxides. The outstanding advantage of the flux is that it acts as a vehicle in which the magnesium oxide product is suspended, thereby enabling a clean separation of this material from the metal phase.

Complete reductions have been achieved at temperatures as low as 650°C, with the reduction rate increasing rapidly as the temperature is raised.[22] Reduction rate also was observed to increase with a decrease in oxide particle size.

Although the reduction of uranium oxides by zinc-magnesium alloy in the presence of flux is being investigated at ANL primarily as a step in the pyrometallurgical fuel-recovery process, it has potential application to the reduction of uranium oxide to metal in feed-material production. The successful demonstration of this technique has prompted application of the procedure to other compounds. Essentially complete reductions of uranium tetrafluoride and plutonium dioxide have been achieved.[22]

Electrolytic Refining of Uranium

Routine production techniques have been developed at ANL[23] to supply high-purity uranium by electrolytic refining of the metal in fused salt. The primary operations used in the preparation of high-purity uranium ingots were (1) deposition of the electrolytic crystals in a fused-salt bath; (2) preparing the crystals for melting by cutting to size, followed by washing to remove adherent electrolyte, and cleaning by nitric acid pickling; and (3) melting the crystals and casting the metal under high-vacuum conditions.

A schematic drawing of the main production Hastelloy C cell, which measured 20 in. in diameter by 36 in. deep, is shown in Fig. V-3. The cell was designed to provide a positive pressure of argon over the fused-salt bath. A charge of approximately 450 lb of electrolyte (nominally 32 wt.% lithium chloride, 38 wt.% potassium chloride, and 30 wt.% uranium tetrafluoride) was kept at a temperature of from 440 to 450°C. The cell was provided with six uranium anodes 1.1 in. in diameter by 24 in. long. The cathode was a 3-in.-diameter by 36-in.-long zirconium tube.

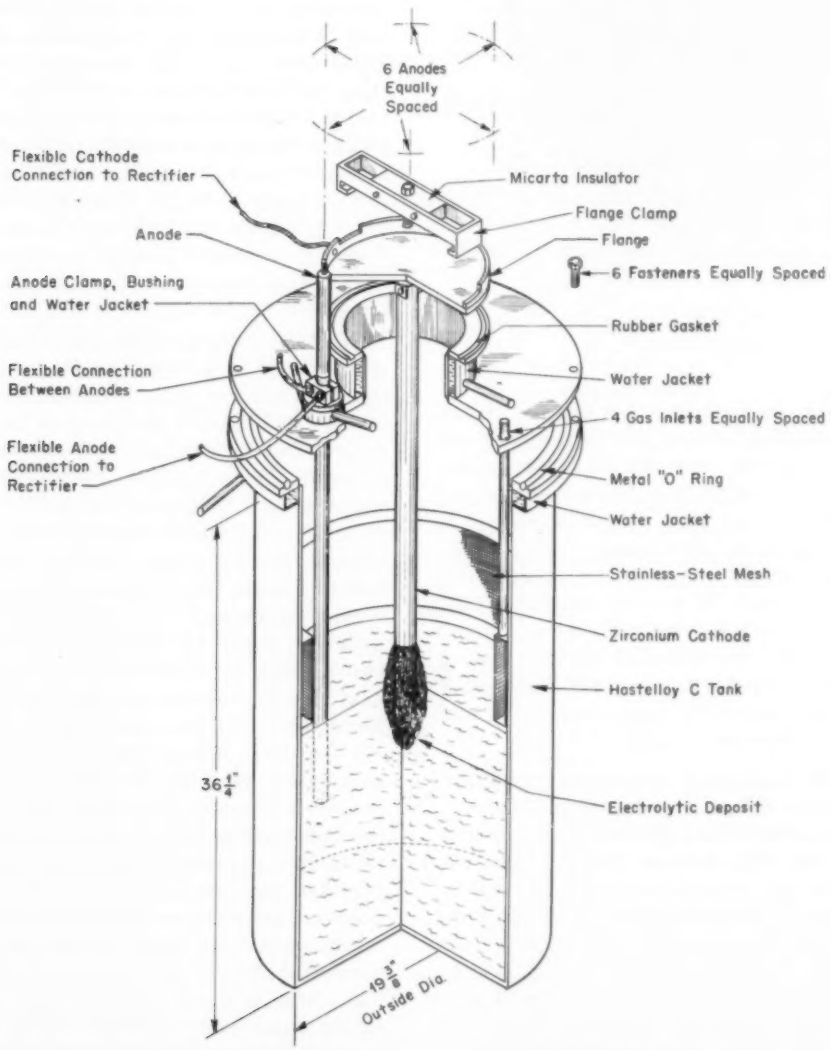

Fig. V-3 Large Hastelloy C electrolytic cell.[23]

Fig. V-4 Typical electrolytic uranium deposit obtained from the Hastelloy C cell.[23]

At the start of electrolysis, a current of 250 amp was applied to the cell. As deposition proceeded, the current was reduced to approximately 20 amp at 0.35 to 0.50 volt. The electrolytic cell was operated on a schedule to produce 10 kg of purified uranium per month. The crystal deposit (Fig. V-4) was removed from the cell every 72 hr; the weight of individual pulls of electrodeposited metal ranged from 3 to 4 kg. Periodic salt additions were required during continuous operation. Approximately 70 per cent of the input anode stock was recovered as deposited crystal.

The crystalline metal deposit was removed from the cell and transferred to a milling machine. During the cutting operation, the crystals were kept wet with distilled water to prevent burning. The cut crystals were washed for 2 hr in warm water and then pickled in 25 vol.% nitric acid. The clean crystals were vacuum dried and cast into uranium ingots. The high-purity ingots consistently contained less than 70 ppm total analyzed impurities. Considerable metal was lost by reaction of the crystals with water during washing and by nitric acid during pickling. It was estimated that about 20 per cent of the anode stock was removed as usable high-purity uranium ingots.

Recovery of Magnesium and Fluoride Values from Magnesium Fluoride Slag

In the production of uranium metal by reaction of uranium tetrafluoride with magnesium, the large quantities of magnesium fluoride slag which are produced may contain up to 7 per cent uranium. The uranium value is recovered at the Feed Materials Production Center, Fernald, Ohio, by grinding the slag and leaching with hydrochloric acid.[6] The insoluble magnesium fluoride is discarded. At present, the uranium values bear the burden of cost in processing the slag. Since magnesium and fluoride values represent a large portion of the raw-material costs in the production of uranium metal, the recovery of these values, presently discarded, might result in large savings. Magnesium metal would be recycled to the reduction of uranium tetrafluoride. Hydrogen fluoride could be employed in the conversion of uranium dioxide to uranium tetrafluoride.

An electrolytic procedure has been developed at Fernald[24] to produce magnesium metal and hydrogen fluoride from a fused electrolyte containing 27.9 mole % magnesium fluoride, 13.1 mole % calcium fluoride, and 59 mole % lithium fluoride. The cell was operated at an electrolyte temperature of approximately 780°C. Molten magnesium metal collected at a mild-steel cathode. During initial work it was observed that the anode product, fluorine, generally attacked the anode to form fluorides of the anode material. Since no suitably resistant material was found to withstand this corrosion, attention was directed toward developing a hydrogen-saturated anode that would yield hydrogen fluoride product. Although this approach was more successful, considerable anode corrosion was observed in small-scale pilot tests. The hydrogen electrode required excessively high voltages to drive a current through the dielectric and perform the electrolysis. During most of the demonstration tests, the over-all current efficiency of the cell, based on the quantity of magnesium produced, was not more than 16 per cent. The purity of the magnesium metal was as high as 99.6 per cent; however, metal with a high concentration of impurities was produced when a fresh electrolyte was used.

Electrorefining of Thorium Metal

In reactor-grade thorium there are strict limitations on the amounts of impurities which have a high thermal-neutron absorption cross section such as cadmium and some of the rare earths. The specification is more relaxed with respect to such elements as carbon, oxygen, iron, and silicon, although it is known that certain of these impurities, specifically carbon, in concentrations up to 100 ppm increase the hardness of the metal considerably.

An electrorefining process for producing reactor-grade thorium has been described by Kachi et al.[25] The electrolyte used in this process was a molten salt containing 30 wt.% thorium tetrachloride in a eutectic mixture of sodium chloride and potassium chloride. Briquettes of impure thorium metal served as the anode, and a molybdenum rod immersed in the electrolyte was the cathode. The cathode was separated from the anode by a stainless-steel screen that limited contamination of the cathode deposit. The impure thorium anodes were prepared by electrolysis of impure potassium-thorium fluoride ($KThF_4$) dissolved in a potassium chloride–sodium chloride eutectic at 780°C. The cathode deposits were washed with water and compacted into briquettes for feed to the refining cell.

The refining cell was operated at a temperature of 750 to 800°C with an applied voltage of 0.5 to 0.8 volt. The current yield efficiency was about 70 per cent. High-quality thorium metal crystals were produced under conditions of low anode current density. The average crystal size of the deposit was approximately 15×20 mm and had an average hardness of 35 (Vickers hardness, 50-g load). The content of analyzed impurities in the refined metal was approximately 200 ppm, of which the rare earths contributed less than 50 ppm.

An observation on the fundamental behavior of thorium ions at the cathode during electrolysis from lithium chloride–potassium chloride or sodium chloride–potassium chloride eutectics has been published recently.[26] Of specific interest was the investigation of the polarization of a thorium cathode during the simultaneous deposition of thorium and alkali metals on the cathode. It was observed that the thorium potential changes little with the cathode current density up to 0.01 amp/cm^2. Under such conditions alkali metal is able to diffuse into the thorium metal phase and does not accumulate on the thorium surface. At higher current densities the cathode potential increases sharply, and the slowness of diffusion of alkali metal into the thorium deposit leads to accumulation of the metal in the thorium surface layer. It was concluded that the role of alkali metal ions and chloride anions is to transfer the electric current through the melt, and these ions do not participate in electrode processes until the electrolyte layer next to the cathode is completely depleted in thorium ions.

Additional Review References

A second edition of C. A. Hampel's *Rare Metals Handbook*[27] has been recently published. This new edition presents recent information and data on over 34 elements, including complete chapters on uranium, thorium, and plutonium. Additional information on metals and ceramic materials of application to the atomic energy program may be found in reference 28.

The AEC has translated a Russian text that is devoted to the theoretical principle underlying the processes for treating uranium ore concentrates to produce pure uranium salts and uranium metal.[29] Data published through 1958 have been utilized in the text, and the extensive referencing of foreign publications makes this book an unusual source of information on uranium processing.

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Section

VI

Reactor Fuel Processing

Safety in Fuel Processing

Safety precautions utilized for criticality control and confinement of fissionable and radioactive materials in various aqueous processing operations performed at the ICPP have been described by Morrison.[1] The ICPP is designed to process highly enriched uranium fuels from various types of reactors. Three primary nuclear safety controls are used: (1) geometrical: wherever practical the vessels are designed to be geometrically safe under process conditions; (2) batch or mass limitation: a limit is placed on the quantity of uranium that may be contained in a vessel or cell; and (3) concentration limit: this control is used in conjunction with batch limitation and places a limit on the quantity of uranium per unit volume in a vessel.

The original plant design and later additions and modifications included built-in geometrical control wherever practical, with allowances for possible neutron interaction between vessels. The ICPP was designed for direct maintenance. Economics of constructing and operating the plant prohibited designs that would be geometrically safe in all respects or one that would process completely batches that were less than minimum critical mass. Prevention of a nuclear or radiation incident is complicated by the large number of vessels and interconnecting piping. Constant awareness of the potential danger by all personnel is therefore necessary to maintain nuclear safety in the ICPP operations. Operations are performed according to standard operating procedures which are designed to avoid circumvention of the primary nuclear safety controls. These procedures give mass and concentration limits for certain operations which involve appreciable quantities of uranium. Administrative control is necessary to ensure compliance with standard operating procedures.

During aqueous processing operations, suitable safeguards or provisions must be made to ensure that uranium will not precipitate either as a result of evaporation or addition of reagents. These considerations are used in establishing batch limits on the dissolvers. Limits are usually set low enough so that there is little possibility of a nuclear incident resulting if a slurry or a concentrated solution of uranium is transferred to a tank where a critical slab geometry can result. Occasional transfers of uranium-rich recycle solutions are made under strict administrative control supplemented by a system of valve lockouts.

Neutron-absorbing materials are not used as a primary nuclear safety control at the ICPP; however, there are several applications where this principle is used in the plant to increase the margin of safety. The potential usefulness of vessels filled with neutron absorbers is well recognized and undoubtedly will be relied on in the future as a primary control, as more experimental data are obtained.

Operator training and supervision are a very important part of the ICPP nuclear safety program. Regardless of training, ability, procedures, or experience, the human factor will show up in some unexpected incident or place and usually when least expected. The most common error is in assuming rather than verifying.

The possibility has frequently been discussed that, for a comparatively small increase in building costs, it would be possible to include sufficient "as-built" shielding in a process plant to prevent serious radiation damage to an operator in the event of a critical excursion. In a United Kingdom report[2] issued in 1960, the effects of as-built shielding and also the effect of prompt operator action in evacuating the building are evaluated for a nuclear incident.

The examination of a number of nuclear excursions which have occurred suggests that there is a wide variety of conditions that result in excursions of about 10^{17} fissions. This figure of 10^{17} fissions is considered to cover most conditions where criticality in plant processes occurs by accidental precipitation, water addition, or similar means. It is well known that certain supercritical systems can continue to "chug" at frequent intervals until some relieving mechanism, such as evaporation, dilution, slow moderator or reflector loss, renders the system subcritical. For this analysis, however, the authors defined a "standard" incident as one of 10^{17} fissions in a single burst with the total energy release completed in 1 sec.

The prompt gamma dose and the neutron dose were computed for an operator at various distances from an incident and for various as-built shields (steel and concrete being the normal structural materials). The following table gives the distances at which an operator, shielded by different thicknesses of as-built shielding, will receive no more than the indicated levels of radiation.

Dose, r	Distance (in feet) of operator from source of radiation for indicated shielding thickness		
	1-in. steel	6-in. steel	12-in. steel
500 (50% lethal)	13	9	6½
25 (accidental exposure)	59	40	26½
12 (emergency exposure)	84	57	37½

In addition, the calculations show that each 1 ft of ordinary concrete (density = 2.5 g/cm^3) reduces the dose by approximately a factor of 10. If an operator is to receive not more than the emergency exposure of 12 r from a single excursion of 10^{17} fissions when only a concrete wall separates him from the critical vessel, the concrete wall must be 3 ft thick. In this respect the as-built shielding in high-activity-level, and most medium-level, radiochemical plants will provide sufficient safeguard.

Figure VI-1 illustrates the fission-product gamma dose (integrated) as a function of time for a case in which the operator is assumed to hesitate 2 sec and run directly away from the incident at a speed of 15 ft/sec for the first 50 yd. The distances shown in the graph refer to the original distance of the operator from the incident when it occurs. No shielding is assumed. Comparison of these data with other data given in the original report shows that prompt evacuation by the operator can reduce the dose received from fission-product gammas by a factor of 2 or 3.

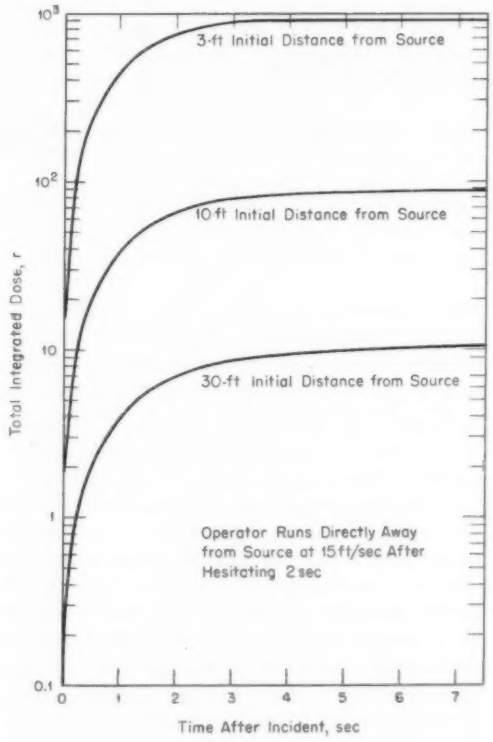

Fig. VI-1 Fission-product gamma dose received by an operator present at an accidental nuclear excursion.

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